Y-1852
Part 2

NERVA FUEL ELEMENT DEVELOPMENT PROGRAM SUMMARY REPORT - JULY 1966 THROUGH JUNE 1972

Impregnation Studies

UNION CARBIDE

OAK RIDGE Y-12 PLANT
OAK RIDGE, TENNESSEE

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Impregnation Studies

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This report presents a summary of work performed on the impregnation of NERVA Fuel Elements for the Space Nuclear Systems Office, under Purchase Orders SNC-51, SNC-73, SNC-81, and SNC-95 during the period July 1966 through June 1972.

Prepared for the U.S. Atomic Energy Commission
Under U.S. Government Contract W-7405-eng-26

ABSTRACT

Two methods were employed to densify graphite bodies: gaseous impregnation and liquid impregnation. Gaseous impregnation consisted of two processes: direct flow and pulse vacuum. Liquid impregnation was based on the use of a polymer of cinnamylideneindene.

Both types of gaseous impregnation processes were successful in densifying the fuel element graphites; however, the process time of the pulse-vacuum method was shown to be significantly shorter than that of the direct-flow process. The liquid impregnation process was also successful. Two to four impregnation cycles were required to obtain a maximum density.

CONTENTS

FOREWORD

The NERVA graphite fuel element program, which was funded for several years by the Space Nuclear Systems office, has been terminated at the Oak Ridge Y-12 Plant.[a] This report was abstracted from a series of progress reports which were routinely issued during the course of the fuel element studies, and covers data collected during the investigation leading to the manufacture of isotropic, high coefficient of thermal expansion graphite bodies using molding techniques.

(a) Operated by the Union Carbide Corporation's Nuclear Division for the US Atomic Energy Commission.

SUMMARY

Various types of graphites were manufactured during the NERVA fuel element development program to obtain data on the effects of fillers and binders, and to characterize the physical properties of a variety of graphites. These graphites ranged structurally from near isotropic to anisotropic. Open porosities of the before-impregnated bodies were generally 16 to 20 percent with bulk densities being dependent on the filler, binder, and other process conditions. A density range of 1.60 to 1.80 gms/cc was typical for most of the unimpregnated graphites.

An increased bulk density was desirable in order to obtain a high carbon concentration and increase the physical property values. Accomplishments that were realized in this phase of the program are summarized in the sections that follow.

GASEOUS IMPREGNATION

Direct-Flow Method

1. An argon-1,3-butadiene gas mixture was used to increase the density of graphite fuel elements from 1.70 to 1.84 gms/cc at a temperature of 750°C and a process time of 100 hours. Flexural strengths also increased (from 5,600 psi before densification to 8,100 psi after densification).

2. An argon-methane gas mixture was used to increase the density of fuel elements from 1.70 to 1.90 gms/cc at a process temperature of 950°C and a process time of approximately 140 hours.

Pulse-Vacuum Method

1. A laboratory furnace capable of pulse-vacuum operation was scaled in size to permit preproduction-type operations to be conducted.

2. Using 1,3-butadiene gas, pulse-vacuum cycle consisting of a 1-second pressure at 2 psig, followed by a 4-second vacuum to 27 inches of mercury at a temperature of 720°C produced density changes of 1.70 to 1.90 gms/cc within a process time of less than 30 hours.

LIQUID IMPREGNATION

1. A polymer of cinnamylideneindene (CAI) was developed for use as a liquid impregnant for graphite bodies.

2. Two to four impregnations were required to increase the graphite density from 1.70 to 1.90 gms/cc.

INTRODUCTION

The NERVA graphite fuel element program, over a period of several years, has been directed toward the goal of a very-high-specific-impulse engine. One of the recent objectives has been to produce a reactor capable of operating up to 60 cycles with run durations of ten minutes per cycle and at an exit gas temperature of at least 2,400°C. As part of the development program for this engine, graphite fuel element technology was explored.

A NERVA graphite fuel element is extruded from a mixture containing carbon or graphite powder, pyrocarbon-coated uranium dicarbide fuel beads, and a resin binder. The extruded shape is in the form of a hexagonal rod having a nominal cross-flats dimension of 0.800 inch and a length of 60 inches. Each fuel element contains 19 holes having a nominal diameter of 0.100 inch. The hole locations are carefully defined by the fuel element specifications. After extrusion, the element is baked to 250°C in air, then heated to 850 and 2,200°C. Impregnation of the element may be performed before or after the final heat treatment to 2,200°C. For this report, the fuel element matrix is considered to be the carbon or graphite structure used to hold the fuel beads.

The 2,200°C heat-treated element is later processed through a series of manufacturing steps to achieve a final hexagonal shape with an across-flats dimension of 0.7520/0.7540 inch and a length of 52 inches. All of the gas holes are coated with a thin film of a metal carbide. The carbide thickness along the bore length was specified, but thicknesses of 3 ± 0.5 mils were common.

During the program, routine biweekly and quarterly reports on the development program were prepared. These documents included a description of the results of the investigation to impregnate the graphite bodies in order to obtain higher carbon densities, increased strength, and other desirable physical properties.

This report is a compilation of impregnation data, previously reported, during the course of the studies. Selected portions from a variety of reports have been abstracted to form this report. Abstracted reports on several other phases of the program can also be obtained in reports Y-1852, Part 1, Y-1852, Parts 3 through 5, Y-1857, and Y-1868.

GRAPHITE IMPREGNATION

GASEOUS IMPREGNATION

Direct-Flow Impregnation

1,3-Butadiene - A gas impregnation technique which was evaluated is the direct-flow method in which a mixture of 97 percent argon and three percent 1,3-butadiene gases were passed through the element bores at ambient pressure.[1,2] This method relies on the diffusion of butadiene gas into the element matrix and is slower than the pulse-vacuum method described later. The experimental data are summarized in Table 1. The equipment that was used for these tests was the standard metal carbide bore-coating furnace. Full-length element matrices could be impregnated in this furnace. However, as noted in Table 1, run times in excess of 100 hours were required at plating temperatures of 750°C. The impregnated element surfaces were usually sealed with a thin film of pyrocarbon at overall densities near 1.84 gms/cc.

Table 1

DIRECT-FLOW IMPREGNATION WITH THREE PERCENT BUTADIENE-97 PERCENT ARGON GAS MIXTURE AT 750° C

Run	Matrix	Density (gms/cc) Before Impregnation	Density (gms/cc) After Impregnation	Impregnation Time (hrs)
1	GL 1008 filler, ITX-ACN binder, Type 01 element, no fibers.	1.70	1.82	101
2	Same as Run 1 except that 0.5% fibers were added to the matrix.	1.70	1.82	101
3	Same as Run 1 except that 1% fibers were added to the matrix.	1.70	1.82	101
4	Santa Maria filler, ITX-ACN binder, 19-hole unloaded element, no fibers.	1.70	1.84	116

Flexural Strength - Fuel elements were manufactured using several types of graphite fillers. One type of element was made using an isotropic filler, obtained under the name of Santa Maria Coke (SMC), which is produced by Collier Carbon and Chemical Corporation.

The flexural strength of the Santa Maria-type fuel elements were determined. The strength prior to impregnation had an average value of 5,600 psi at a density of 1.70 gms/cc. After impregnating the graphite matrix to a density of 1.84 gms/cc, the flexural strength was increased to 8,100 psi, as reported in Table 2.

Coefficient of Thermal Expansion - It is believed that the impregnant was deposited in the element matrix in a random and, therefore, isotropic manner. Thus, the coefficient of thermal expansion (CTE) of the element would be expected to increase or remain near the original value. Santa Maria elements prior to impregnation had a measured CTE value of 6.1 x 10^{-6}/°C (25 - 1,000°C). After impregnation, the CTE values of three element pieces were about equal to the values obtained on the nonimpregnated pieces.

Methane - An alternate gas mixture of 97 percent argon and three percent methane was used in some of the direct-flow experiments.[3,4] Elements selected for these initial studies were extruded central-support elements containing GL 1008 fillers bound with isotruxene (ITX). The element matrices contained up to 1 1/2 weight percent phenolic fibers based on the original unfired fiber weights. The amount of impregnant which could be deposited in the elements was approximately 10 weight percent.

Table 2

DENSITY AND FLEXURAL STRENGTH DATA OF PYROCARBON IMPREGNATED ELEMENTS

Element Density[1] (gms/cc)	Flexural Strength (psi)
1.70	5,440
1.78	6,640
1.81	7,720
1.84	8,110

(1) The element was extruded using Santa Maria low-fired coke as a filler and ITX-ACN-I mixture as the binder. The element was gaseous impregnated with butadiene.

Impregnations using methane at atmospheric pressure were made at both 850 and 900°C. The methane partial pressure was 25 mm mercury; the total gas flow per element was 8 liters/minute using argon as the diluent. Figure 1 presents a graph of the weight gain as a function of the coating time. These data show that after 115 hours and 850°C, a 1.5 weight percent gain per element was obtained. At a temperature of 900°C, a faster deposition rate was obtained (4 wt % in 141 hours). For comparison, typical pulse-vacuum data are included in the graph.

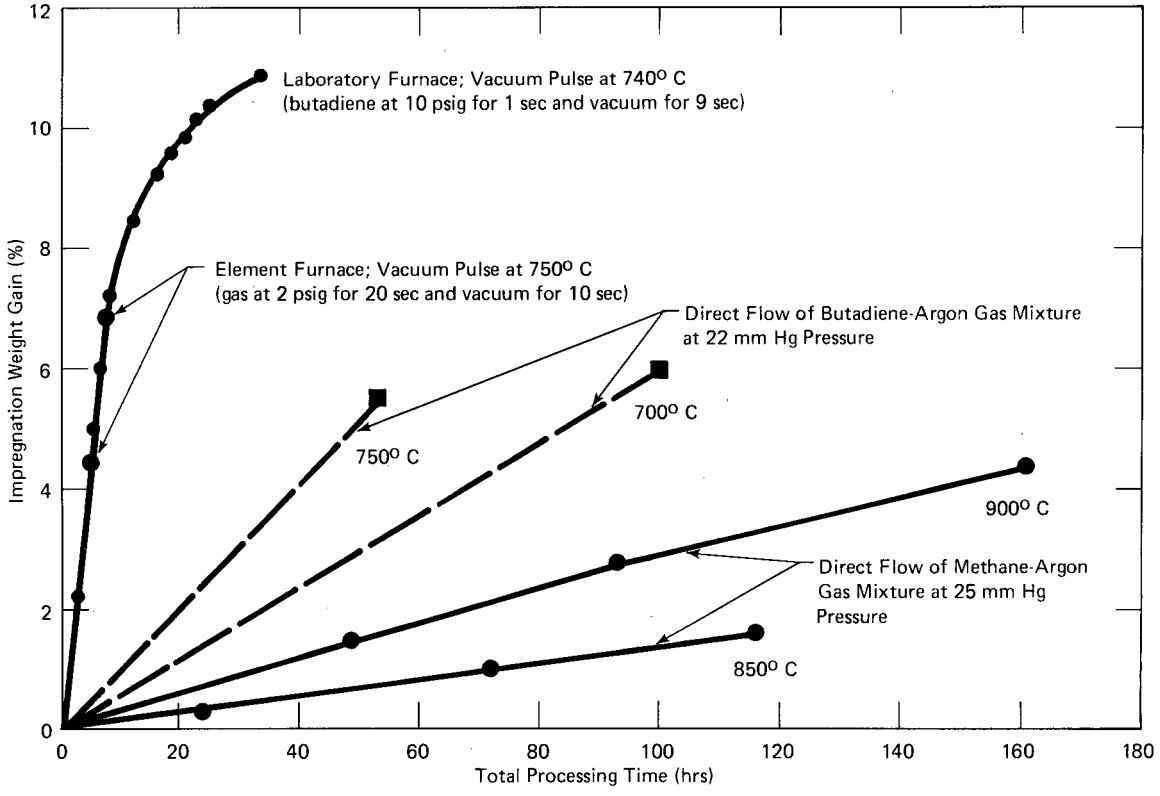


Figure 1. GAS IMPREGNATION OF ELEMENTS UNDER VARIOUS CONDITIONS. (ITX-ACN Bound Santa Maria Coke)

Pulse-Vacuum Impregnation

An investigation was made of the impregnation of graphite bodies by thermal decomposition of 1,3-butadiene gas using pulse-vacuum techniques.[5 - 7] This work included studying the deposition rate as a function of the number of pulse-vacuum time cycles and also the rate as a function of temperature. The optimum conditions found during these studies were a pulse of one-second at a pressure of two psig followed by a four-second vacuum to 27 inches of mercury at a temperature of 720° C.

Pulse Vacuum Equipment - The laboratory coating equipment used by Beatty and Kiplinger[5] was used to successfully densify ITX-ACN (acenaphthalene)-bound SMC matrices (up to densities of 1.90 gms/cc). This equipment was capable of impregnating pieces having a length of about five inches.

Because of the small size of the laboratory furnace, an existing bore-coating furnace was modified to permit pulse-vacuum impregnations of ten elements per run. These changes allowed the equipment to be operated with cycle times as low as a 0.5-second pressure and a 4.5-second vacuum. Longer cycle times were permissible.

A pulse-vacuum cycle was operated at a 0.5-second pressure to 2 psig and a 4.5-second vacuum to 27 inches mercury. The furnace center temperature was controlled at 720°C. However, due to a temperature profile problem, the furnace top could only be operated at 650°C.

At or about four inches from the furnace top (element gas inlet end), the furnace temperature was approximately 710°C and remained at 710 to 720°C to within about four inches of the exit end. The furnace temperature at the exit end was normally approximately 700°C. Even with this temperature gradient, the elements were uniformly filled with carbon.

No major problems occurred while using the modified bore coating equipment. The gas inlet valves operated satisfactorily, but the vacuum valve had to be taken out and cleaned to remove tar and oil after each 30-hour run. This valve was radically modified during the course of these studies by changing the plastic valve seats to brass seats and strengthening the valve stem and other parts of the body in order to obtain a longer valve life. A persistent minor problem was caused by trace impurities in the argon purge gas which was used for cool-down operations. These impurities attacked the zirconium carbide-carbon composite-type elements quite readily, but did not show a problem with graphite elements since they are more resistant to attack. An argon purifier was installed on the inlet supply; but, due to the many pipe connections and graphite fixtures, the possibility of in leakage of trace amounts of oxygen did exist. The latest run data indicated that the LASL uranium carbide-zirconium carbide-carbon element (composite element) pieces could be impregnated without major oxidation of the element. However, if composite elements are to be routinely impregnated, it is believed that a preheater made of composite elements would need to be installed in the furnace. This modification would not pose a problem since there is adequate space to install this type of preheater in the furnace.

Laboratory Experiments - Early experiments used 1,3-butadiene gas for the element impregnation studies. The impregnation temperature was varied; most of the tests were made at 740°C. Laboratory equipment used for the impregnations at that time only accommodated specimen lengths up to five inches.

All element matrices were extruded using isotruxene-acenaphthylene-indene (ITX-ACN-I) as a binder.[8] This material produced a graphitic residue, and the elements normally had densities near 1.70 gms/cc and up to 20 percent open porosity. For the pulse-vacuum impregnation studies, matrices were also extruded with chopped green fibers in an endeavor to further increase the flexural strength.

Table 3 provides a summation of the matrices impregnated in this experimental group. These data show that densities of 1.9 gms/cc were achieved using impregnation times of up to 35 hours. Matrices containing both GL 1008 and Santa Maria coke fillers have been densified. After densities of above 1.85 gms/cc were achieved, the fuel element body leak rate decreased sharply to less than 170 cc/min, which was the maximum specified level. Some surface sealing of the open pores at the matrix surface could have occurred.

Table 3

PULSE-VACUUM IMPREGNATION WITH 1,3-BUTADIENE GAS AT 740°C

Run	Matrix	Density (gms/cc) Before Impregnation	Density (gms/cc) After Impregnation	Impregnation Time (hrs)
1	GL 1008, ITX-ACN binder, Type 01 element, no fibers.	1.70	1.9	26
1a	Same as Run 1.	1.70	1.83	11
2	Same as Run 1, but with 0.5% fibers added to the matrix.	1.70	1.89	35
3	Same as Run 1, but with 1% fibers added to the matrix.	1.70	1.86	16
4	Same as Run 1, but with 1 1/2% fibers added to the matrix.	1.70	1.9	34
5	Santa Maria filler, ITX-ACN binder, Type 01 element, no fibers.	1.70	1.84	11
5a	Same as Run 5.	1.70	1.87	30
6	Same as Run 5, but with 1% fibers added to the matrix.	1.70	1.89	15

These first experiments had shown that element matrices could be densified using a cycle of one second at a 10-psig pressure and ten seconds at a vacuum of 25 inches of mercury at a temperature of 740°C. Both SMC and GL 1008 matrices, bound with ITX-ACN, were densified. Central-support element pieces having nominal 1/4-inch webs were also uniformly densified with little evidence of surface sealing. Radiographs of impregnated wafer pieces filled with mercury to show the pore network are presented in Figure 2. The central support wafers had no major surface sealing even though the carbon density was increased from 1.7 to 1.9 gms/cc.

Pilot-Plant Studies - POCO AXF Graphite Rods - Rods machined from POCO AXF graphite were selected as a reference material for the impregnation studies.[9] The NERVA fuel element matrices made from primary POCO carbon filler[10] have a structure similar to POCO AXF graphite. The maximum fuel element web thickness between the gap passage holes was less than 70 mils. To obtain data on the depth of penetration and impregnation

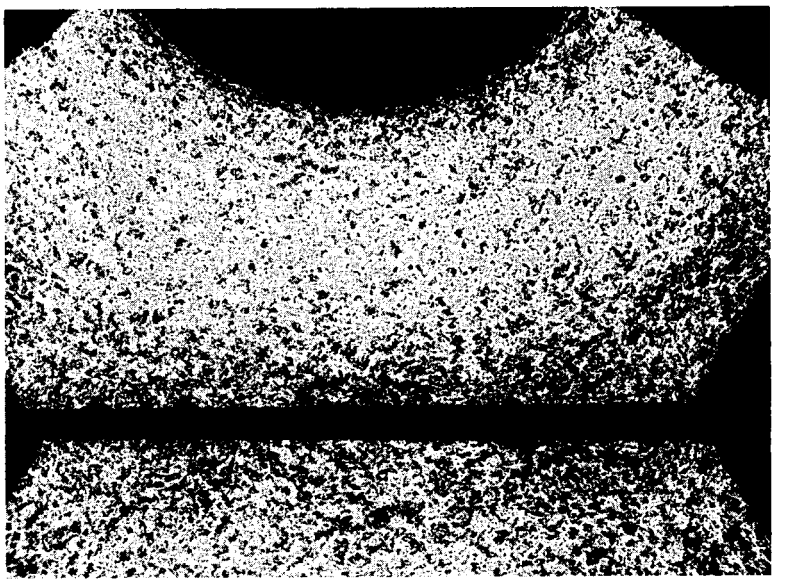


Figure 2. IMPREGNATED CENTRAL SUPPORT ELEMENT. (For this Radiograph, Mercury was Intruded into the Open Pores at 10,000 psia and Radiographed at 35 Kv)

rates, rods having a nominal diameter of 0.250 and 0.500 inch were cut from POCO AXF graphite. These six-inch-long rods were placed at various points along the furnace length. The experimental plan for these runs included variations in the pulse vacuum time cycle and temperature. Impregnation runs were made for time lengths up to the maximum density noted on the test pieces. After a nominal four-hour run, the pieces were measured for density and the run continued. At the maximum density, samples were taken of both rod types (0.250 and 0.500 inch diameter), and the degree of penetration was studied.

One-Half-Second Pressure and 4.5-Second Vacuum - A run was made using the same cycle and conditions as were used on most of the preproduction element studies. A typical plot of density versus time on the 0.500-inch-diameter pieces is given in Figure 3. These data show that the maximum density on the 0.500-inch-diameter rods occurred at about 1.90 gms/cc.

One-Second Pressure and 9-Second Vacuum - An experiment was made at 720°C using a pressure cycle of one second to 2 psig and a vacuum cycle of nine seconds. A typical plot of density versus time on the 0.500-inch-diameter rods is included in Figure 3. Results of the maximum density and the rate of density change were similar to those obtained on the previous run.

Tentative analysis of the data indicated that both the 0.5 second-to-2 psig, 4.5 seconds-to-approximately 27 inches and the 1.0 second-to-2 psig, 9.0 seconds-to-approximately 27 inches runs were about equal. Also, the maximum density and time to maximum density were approximately the same. The degree of penetration was not established, but the density change noted on the 0.250-inch-diameter rods was the same as the change obtained on the 0.500-inch-diameter pieces.

Varying Cycles at Constant Temperature (720°C) - Four pressure-vacuum cycles were studied using a constant temperature of 720°C. Previous work had shown that pressure-vacuum cycles in excess of this temperature tended to deposit a surface seal coat on the graphite. Deposition rates to maximum density for the four runs are reported in the graph of Figure 4. At 720°C, the densest graphite was produced using a 4-second pressure, 4-second vacuum cycle. A one-second pressure, 4-second vacuum cycle was nearly equivalent to the best cycle. Maximum densities were obtained in about 20 hours. Starting densities of the POCO AXF rods varied from 1.79 to 1.87 gms/cc, the average density of all of the rods in the before-impregnation state was 1.83 gms/cc, and the maximum impregnated density was 1.90 gms/cc.

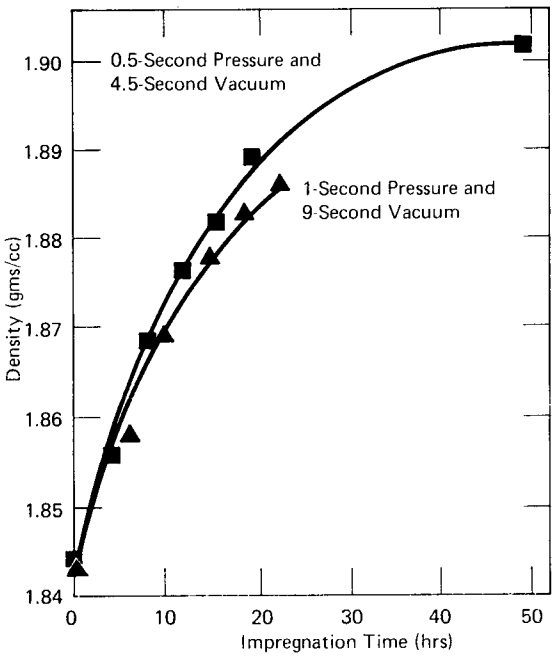


Figure 3. IMPREGNATION RATE ON POCO AXF RODS.

Constant Cycle at Varying Temperatures - Four experiments were made using a constant pressure-vacuum cycle (1-sec pressure-4-sec vacuum) and at four different temperatures (700, 720, 740, and 760°C).[9] Typical rates are shown for each run in Figure 5. These data show that the runs at 720°C produced the fastest deposition rate and also produced the pieces with the greatest density.

Degree of Penetration - Both 1/4 and 1/2-inch-diameter rods were impregnated in each of the impregnation runs. The density of each rod (6 of each type per run) was determined, and the data obtained showed no significant difference in density between these rods. Samples of each type were filled with mercury at varying pressures, then the samples were radiographed to determine the uniformity of the carbon impregnated pieces. The results showed that all cycles and temperatures produced a uniformly dense material, but the pieces impregnated at 760°C had a slight surface sealant.

NERVA Element Scoping Studies - Because of the early pilot-plant furnace limitations, the first scoping runs could not include the 1 and 10-second cycles.[6]

Figure 6 lists the densities obtained at various cycles and temperatures made using the original pilot-plant furnace. A bench-scale run, found to obtain satisfactory results, is also noted.

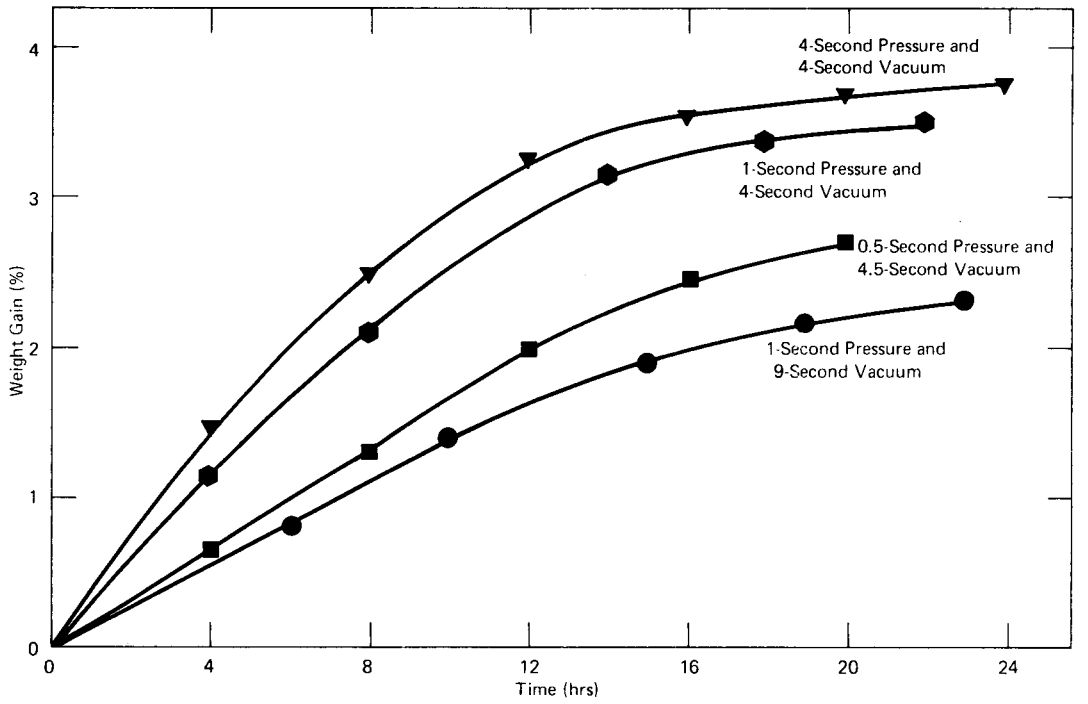


Figure 4. IMPREGNATIONS OF POCO AXF GRAPHITE RODS AT CONSTANT TEMPERATURE, BUT AT VARIOUS CYCLES. (Butadiene Gas at 720°C).

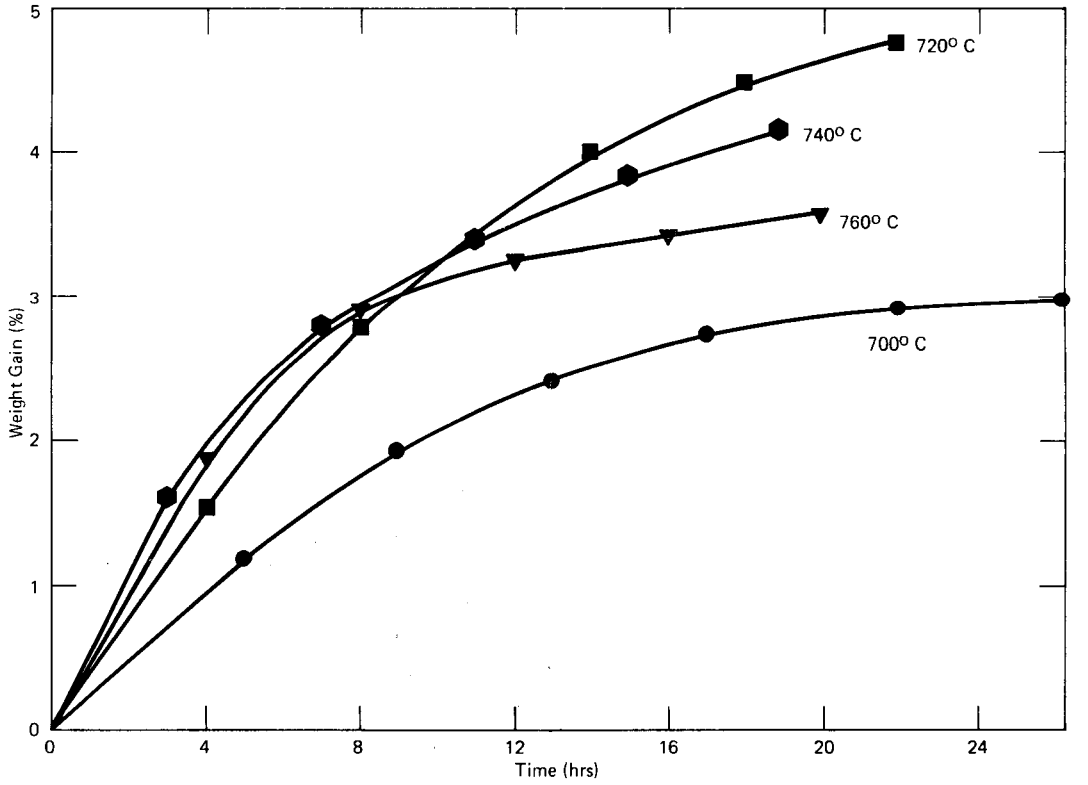


Figure 5. IMPREGNATIONS OF POCO AXF GRAPHITE AT A CONSTANT CYCLE, BUT AT VARIOUS TEMPERATURES. (Butadiene Gas at a One-Second Pressure and a Four-Second Vacuum)

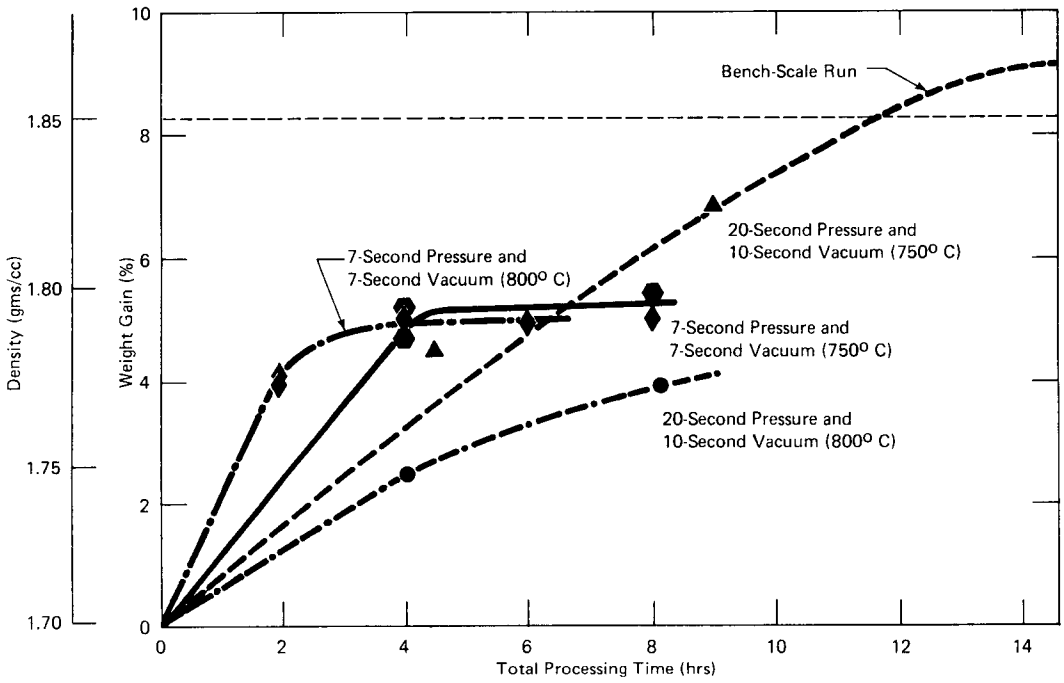


Figure 6. GAS PULSE IMPREGNATION STUDIES.

Scoping Experiments at 750°C - As Figure 6 indicates, cycles of seven seconds of 1,3-butadiene to pressure and seven seconds of vacuum produced a maximum density increase of about five percent (1.7 to ~ 1.78 gms/cc) at times of approximately four hours. Cycles of 20 seconds of 1,3-butadiene pressure and 10 seconds of vacuum produced the same density increase in about the same time (4 hours). Surface sealing occurred and, therefore, runs made for longer times (8 hours) produced no further densification.

Scoping Experiments at 800°C - Runs made at this temperature using a 7-second-pressure and 7-second-vacuum cycle produced a maximum density increase of approximately five percent within two to four hours. Surface sealing was also noted under these conditions.

A run was made at 800°C and a cycle of 20 seconds pressure-10 seconds vacuum. After eight hours, a density increase of four percent was noted without evidence of surface sealing. These run conditions were not studied further because the rate was slower than desired, and it was also believed that some type of abnormal conditions existed in these runs. (Low temperature or an argon inleakage into the chamber could have been the cause of the abnormal results.)

Scoping Experiments at 700°C - Experiments were made to study the results at this temperature at a 7-7 cycle. One run, terminated in one hour due to a lack of

butadiene, increased the element density by one percent. Also, a sooty carbon deposit was observed in the furnace. It is believed that this temperature would produce a soot-like carbon in the matrix pores which would be undesirable.

Primary POCO Fuel Elements - A group of elements previously made in the matrix studies was selected for gaseous impregnation investigations.[7] These elements were made with primary POCO fillers prefired to 1,400, 1,800, and 2,500°C. Each element was bound with ITX-ACN and did not contain Thermax.[10] The elements were impregnated in the 850°C bake state for various time increments to establish the rate per unit time. Samples at the different density levels were taken for thermal stress[11] and other physical property measurements.[12]

Density increases per unit time are reported in Table 4, and a typical impregnation rate curve is presented in Figure 7. As noted in Table 4 and Figure 8, the pore entrance diameter and open porosity decreased as the density increased, which was expected. Metallographs of a typical element are seen in Figure 9. No evidence of surface sealing of the element matrices was apparent.

Table 4

PROPERTIES OF IMPREGNATED PRIMARY POCO ELEMENTS

Element[1]	Impregnation Conditions		Density	Average Pore Entrance Size	Open Porosity
	Temperature (° C)	Time (hrs)	(gms/cc)	(μm)	(%)
000-663-01[2]	730	8	1.73	0.64	19.4
	730	18	1.80	0.51	14.7
	730	27	1.91	0.37	8.5
	720	35	1.92	-	8.5
000-664-01[3]	730	8	1.78	0.63	16.0
	730	18	1.83	0.57	12.1
	730	27	1.91	0.42	8.5
	720	35	1.92	0.43	8.2
000-665-04[4]	730	8	1.74	0.73	16.8
	730	18	1.81	0.61	12.9
	730	27	1.87	0.44	8.6
	720	35	1.88	0.42	8.7

(1) Matrices impregnated in the 850° C bake state and graphitized prior to measurement.
(2) POCO flour prefired to 1,400° C.
(3) POCO flour prefired to 1,800° C.
(4) POCO flour prefired to 2,500° C.

The available data on pulse vacuum impregnation of these types of elements suggest that impregnation times of approximately 30 hours will produce elements of maximum density.

Previous development studies had produced elements made with primary POCO carbon fillers prefired to 1,000, 1,400, 1,800, and 2,500°C. Samples of each element type were graphitized to 2,200°C and their physical properties determined.[13] Element pieces, baked

to 850°C, were gaseous impregnated to various densities using the pulse-vacuum process. The impregnated element sections were fired to 2,200°C prior to determining their physical properties (density, thermal stress resistance, tensile strength, tensile strain, and tensile moduli). These data are listed in Table 5 for the 1,400, 1,800, and 2,500°C fired filler elements.

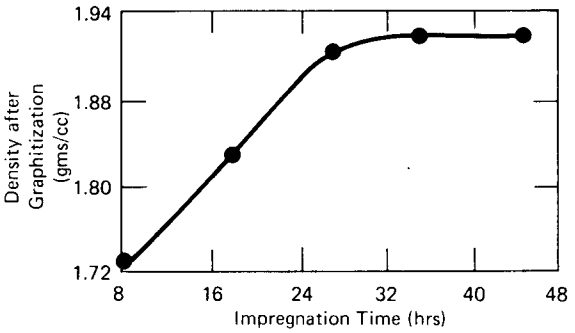


Figure 7. TYPICAL IMPREGNATION RATE OF A PRIMARY POCO FILLER ELEMENT. (Element 000-663-01, a Primary POCO Filler Prefired to 1,400°C)

Primary POCO Filler Prefired to 1,400°C - Extrusion 663 elements were extruded using a flour obtained from POCO ACF graphite which had been processed at 1,400°C. An ITX-ACN mixture was used as the binder in these studies. No Thermax was added to the element matrices. The elements were densified using 1,3-butadiene gas and fired to 2,200°C.

Density - As expected, the density increased as a function of the impregnation time. A maximum density of 1.92 gms/cc was obtained on the nonfueled elements. Due to a temperature gradient in the impregnation furnace, the 74-hour sample showed a slightly lower density increase compared to the 37-hour sample. This sample was located in a slightly cooler region of the furnace (~20°C) than the other samples.

Thermal Stress Resistance - These values, listed in Table 5, were obtained using the ORNL wafer test equipment.[11] As noted, the thermal stress resistance increased with increasing strain, density, and/or other properties.

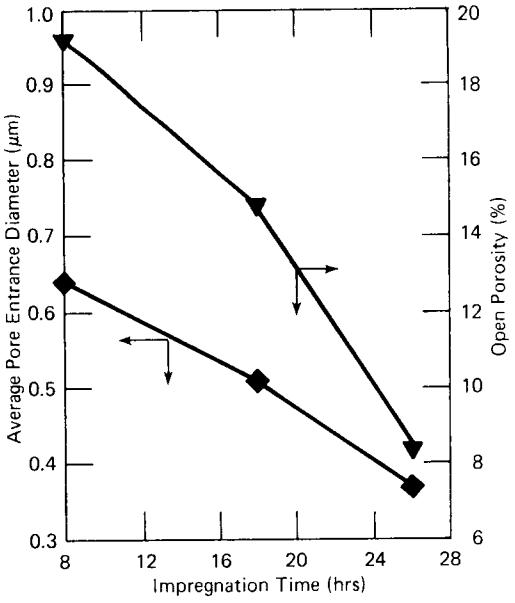
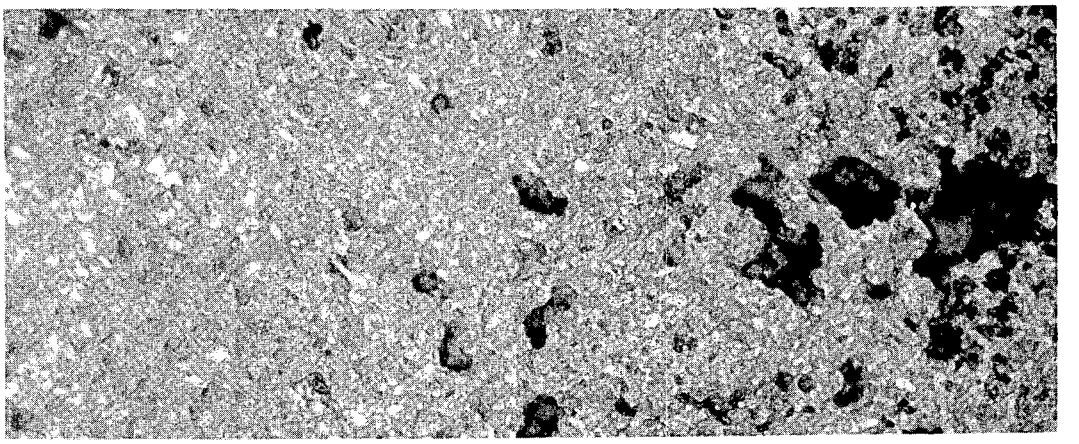


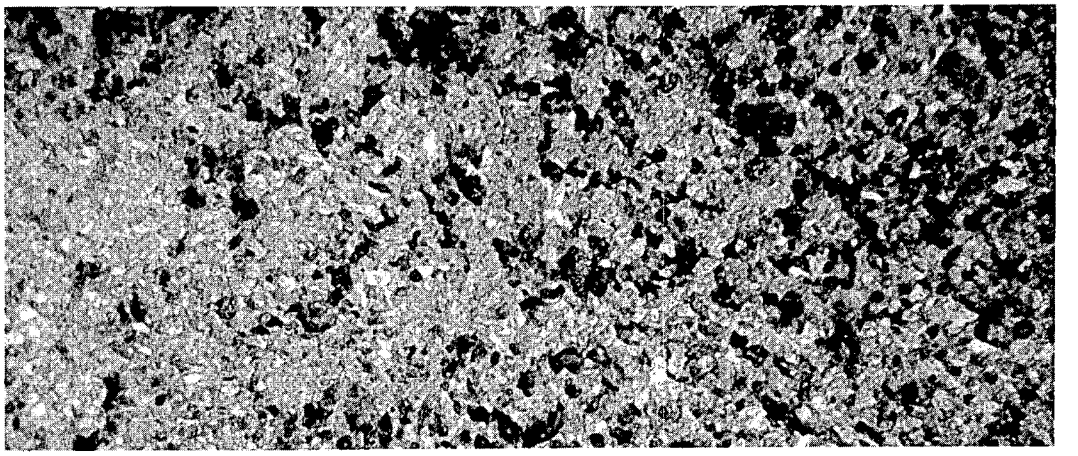
Figure 8. TYPICAL DATA ON PORE ENTRANCE DIAMETER AND OPEN POROSITY.

Tensile Strength - A significant increase in tensile strength was noted on the impregnated samples (Figure 10).

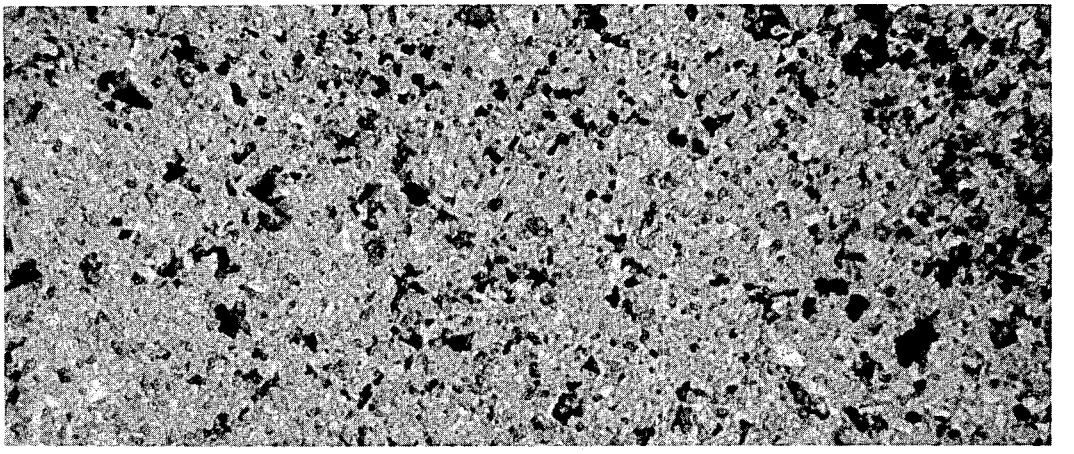
Tensile Strain - Tensile strain-to-failure and tensile-strength values increased linearly as a function of density (Figures 11 and 12). A nominal 0.07 percent strain per 1,000-psi tensile strength was observed on this element group.



(a) Density, 1.78 gms/cc. G836-4b



(b) Density, 1.83 gms/cc. G836-5b



(c) Density, 1.91 gms/cc. G836-6b

Figure 9. A TYPICAL PRIMARY POCO ELEMENT AT VARIOUS IMPREGNATED DENSITIES. (Element 000-664-01, 1,800°C Fired Powder; Sensitive Tint; 500X)

Table 5

PHYSICAL PROPERTIES OF LOW-FIRED POCO FILLERS

Batch	Impregnation Time (hrs)	Density[1] (gms/cc)	Thermal Stress Range (watts)	Tensile Strength (psi)	Ultimate Tensile Strain (%)	Tensile Moduli (x 10^6 psi)	Coefficient of Thermal Expansion[2] (x 10^{-6}/° C)
663[3]	0	1.774	720 - 1,120	2,770	0.165	1.925[4]	7.8
	8	1.720	630 - 640	5,850	0.400	1.52	
	8	-	-	5,250	0.405	1.47	
	18	1.81	760 - 810	7,150	0.476	1.73	
	27	-	-	7,550	0.512	1.74	
	27	1.895	880 - 1,030	8,880	0.517	2.05	
	35	1.92	1,045 - 1,265	7,400	0.478	2.055	
	74	1.90	1,240 - 1,340	8,480	0.566	2.05	
664[5]	0	1.757	630 - 710	3,400	0.2975	1.375	7.0
	8	1.778	820 - 880	5,200	0.390	1.51	
	8	-	-	6,340	0.491	1.55	
	18	1.833	750 - 1,100	8,000	0.573	1.75	
	18	-	-	7,000	0.501	1.67	
	27	1.908	1,040 - 1,200	9,050	0.613	1.85	
	27	-	-	9,520	0.649	1.87	
	35	1.920	1,180 - 1,380	7,560	0.526	1.91	
	74	1.910	1,260 - 1,500	6,900	0.511	1.82	
665[6]	0	1.656	550 - 620	2,520	0.3175	1.02	6.3
	8	1.744	760 - 720	4,420	0.389	1.37	
	8	-	-	4,700	0.416	1.40	
	18	1.805	980 - 1,090	6,270	0.497	1.63	
	27	1.870	840 - 1,020	7,550	0.512	1.81	
	27	-	-	6,960	0.505	1.74	
	35	1.880	940 - 1,140	4,325	0.315	1.73	
	74	1.860	1,100 - 1,150	5,480	0.437	1.68	

(1) Densities did not always increase with increased plating time because of a nonuniform temperature in the gas inlet of the impregnation furnace. The temperature at the "0" region was approximately 30° C cooler than other points. The samples were taken from the element hot-end region and replaced in the impregnation furnace; the cold-end section remained at a constant location in the furnace.

(2) Temperature, 25 to 1,000° C.

(3) Batch contained POCO filler prefired to 1,400° C and gas impregnated in the 850° C element bake state and varying densities. The final graphitization temperature was 2,200° C.

(4) Value believed to be in error.

(5) Batch contained POCO filler prefired to 1,800° C and gas impregnated in the 850° C element bake state. The final graphitization temperature was 2,200° C.

(6) Batch contained POCO filler prefired to 2,500° C and gas impregnated in the 850° C element bake state. The final graphitization temperature was 2,200° C.

Primary POCO Filler Prefired to 1,800°C - Group history of the Extrusion 664 elements was, basically, the same as the Extrusion 663 elements except that the powder was prefired to 1,800°C.

Density - Density increased as a function of the impregnation time. Nominal carbon gain per impregnation hour was about equal to that of the previous element group.

Thermal Stress - Thermal stress resistance values increased with increasing tensile strain, densities, and/or other physical properties (Table 5).

Tensile Strength - A significant gain in tensile strength was noted with increasing densities (Figure 13). Over the density range of 1.80 to 1.90 gms/cc, the tensile strengths increased from 5,800 to 8,800 psi.

Tensile Strain - Tensile strain-to-failure values increased linearly with increasing density (Figure 14). A maximum strain of 0.625 percent was observed on the samples having densities of 1.908 gms/cc.

The tensile strain also increased linearly with increasing tensile strength (Figure 15). A nominal 0.06 percent strain increase per 1,000-psi tensile change was noted on this element group.

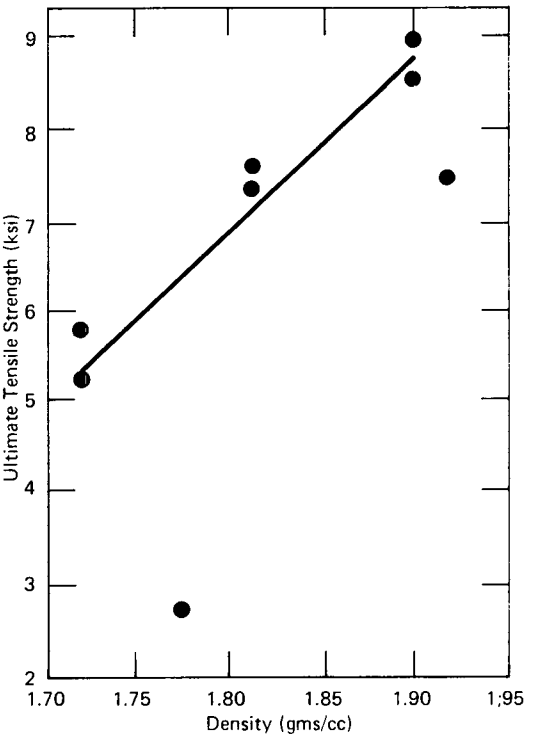


Figure 10. TENSILE STRENGTH AS A FUNCTION OF THE DENSITY FOR EXTRUSION 663 ELEMENTS. (Filler Firing Temperature, 1,400°C)

Primary POCO Filler Prefired to 2,500°C - The manufacturing history of this group was basically the same as that for the two previous groups except that the filler was prefired to 2,500°C.

Density - Densities increased with increasing impregnation times. As usual, the starting density was lower than the other groups. However, past experience has shown that densities and filler firing temperatures are related. The highest initial densities are obtained by using the lowest practical filler firing temperature.

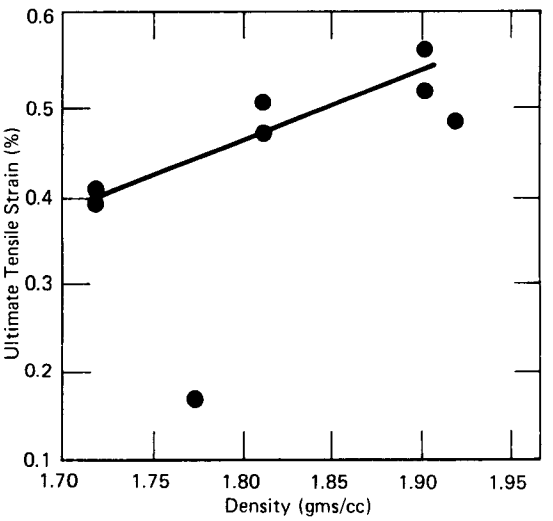


Figure 11. ,TENSILE STRAIN AS A FUNCTION OF THE DENSITY FOR EXTRUSION 663 ELEMENTS. (Filler Firing Temperature, 1,400°C)

Thermal Stress - Thermal stress resistances increased with increasing tensile strain, densities, and/or other physical properties (Table 5).

Tensile Strength - Tensile strengths increased linearly with increasing densities (Figure 16). A density change from 1.71 to 1.81 gms/cc resulted in an increased tensile strength of 3,800 to 5,800 psi.

Tensile Strain - Tensile strain-to-failure values also increased with increasing density (Figure 17), but at a density of 1.87 gms/cc, this group had a strain value of 0.48 percent, whereas the previous group (1,800°C filler firing temperature) showed a strain value of 0.58 percent at the same density.

Tensile strain-to-failure values showed a linear increase with increasing tensile strength (Figure 18). A 0.06 percent change per 1,000-psi tensile strength increase was observed which was about the same as that noted on all three extrusion groups.

Tensile Moduli - It was expected that a density increase would cause a change in the tensile modulus of the specimens. Presented in Figure 19 are data on the test groups which show that an increased modulus change occurred on the densified samples.

A density increase from 1.65 to 1.81 gms/cc caused a modulus change of 1.0 to 1.65 x 10^6 psi with the 1,800 and 2,500°C fired fillers. A density change from 1.81 to 1.91 gms/cc caused a modulus increase from 1.65 to 1.85 x 10^6 psi. The data given in Figure 19 suggest that the 1,400°C fired filler produced a graphite with a slightly higher modulus than the 1,800 and 2,500°C fired fillers.

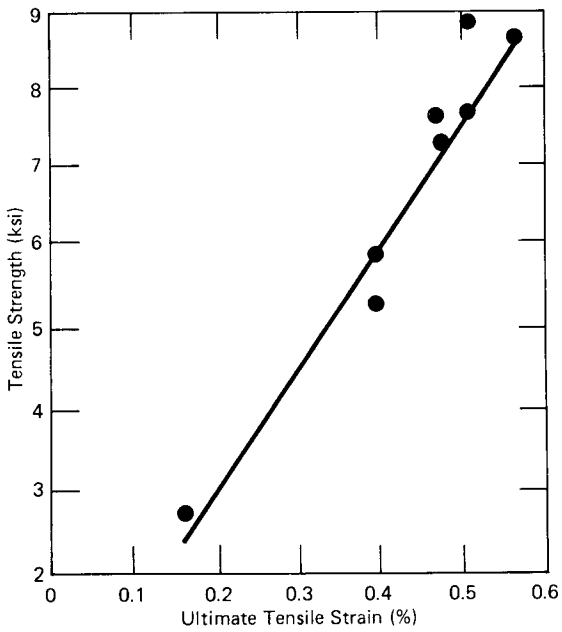


Figure 12. TENSILE STRENGTH AND TENSILE STRAIN FOR EXTRUSION 663 ELEMENTS.

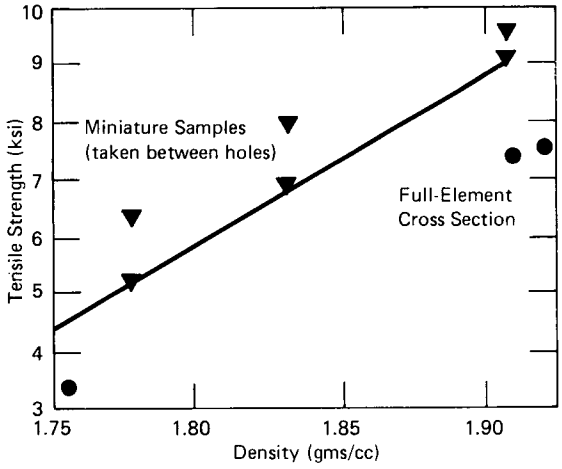


Figure 13. TENSILE STRENGTH AS A FUNCTION OF THE DENSITY FOR EXTRUSION 664 ELEMENTS. (1,800°C POCO Filler Firing Temperature; ITX-ACN Binder; Gas Impregnated)

Santa Maria Coke Elements - During the course of these studies, Santa Maria coke elements loaded with uranium (570 mgs U/cc) were impregnated for various times to establish a rate curve.[7] Basically, two element types were studied which were: (1) graphitized matrices followed by impregnation, and (2) nongraphitized matrices followed by impregnation.

The Santa Maria coke uranium-loaded matrices were first-generation elements, and the bulk density before impregnation varied from element to element. The rate curve of each element type (graphitized and 850°C bake state) was dependent on the original starting element density. However, the data on many elements showed that all had very nearly the same bulk density after a nominal 30-hour impregnation. In other words, if the as-made bulk density was low, the rate per unit time for the first few hours was fast; if the bulk density was high in the as-made state, the rate was low during the first few hours. Typical plots of the impregnation rate versus time for an 850°C bake element and a graphitized element are given in Figures 20 and 21. Data on Santa Maria coke elements indicated that satisfactory densities could be obtained in a nominal 30-hour cycle on uranium-loaded matrices. The 850°C bake element in the as-extruded state, in the partially machined state, and as the graphitized element in the as-extruded and/or machined state can be satisfactorily impregnated.

Thermal Stress Resistance of Nonfueled, Impregnated Santa Maria Coke Elements - Elements made with SMC filler (1,000°C) without Thermax and bound with the ITX-ACN mixture were gaseous impregnated to variable densities.[6] Some of the elements were gaseous impregnated after baking to 2,200°C and were called Type 1 elements; others were impregnated after baking to 850°C and were labelled as Type 2. Those elements which were heat treated to only 850°C were impregnated at 700 and 750°C. The 2,200°C fired elements were gaseous impregnated at 750°C. All elements were impregnated using 1,3-butadiene gas and were given a final heat treatment of 2,200°C prior to testing.

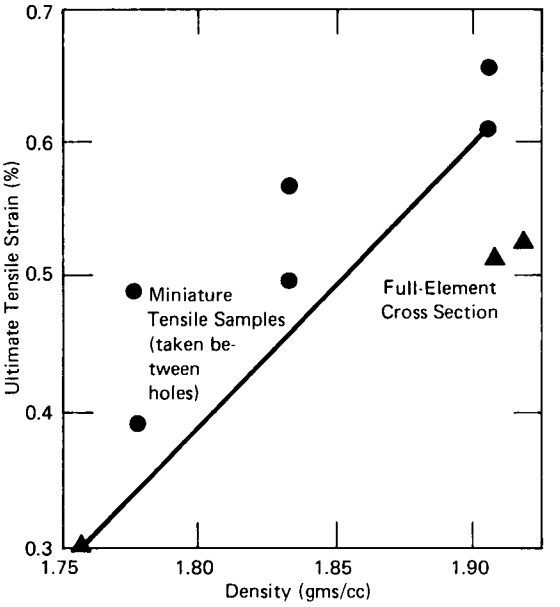


Figure 14. TENSILE STRAIN AS A FUNCTION OF THE DENSITY FOR EXTRUSION 664 ELEMENTS. (1,800°C POCO Filler Firing Temperature; ITX-ACN Binder; Gas Impregnated)

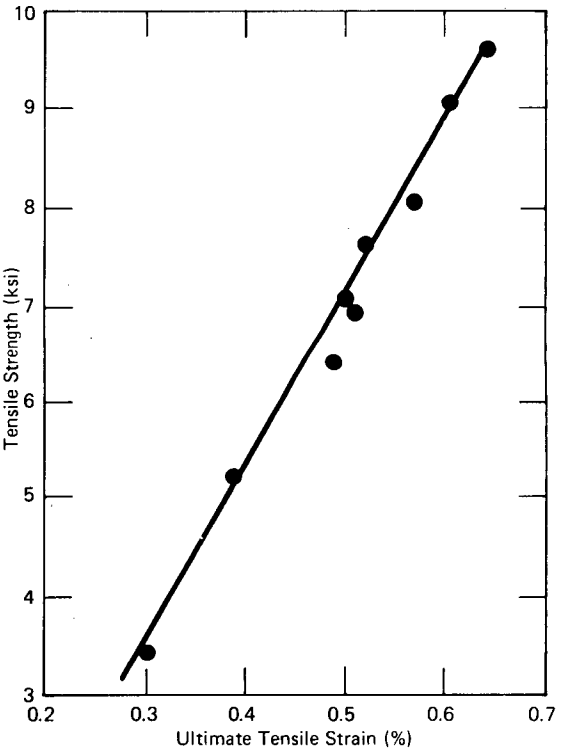


Figure 15. TENSILE STRENGTH AND TENSILE STRAIN FOR EXTRUSION 664 ELEMENTS.

The thermal stress specimens were machined from extruded elements and were 0.100 ± 0.01 inch thick. Twenty wafers per extrusion batch were examined. The thermal stress test

consisted of striking an input-power-controlled arc from a welding machine onto the center hole of the wafer. Power to the machine was preset prior to the arc. Data collected consisted of the power, in watts, which struck the wafer. The power was progressively raised until breakage of the wafers occurred.[11] In no case was a wafer struck with the arc more than one time. The reference material used in these tests was a Pewee 2 element made with POCO AXF-Thermax filler and bound with Varcum.

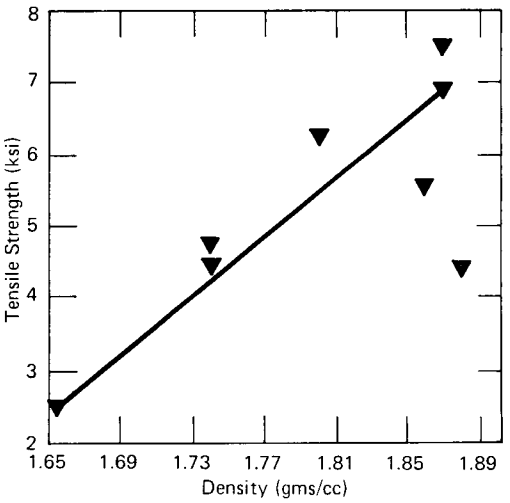


Figure 16. TENSILE STRENGTH AS A FUNCTION OF THE DENSITY FOR EXTRUSION 665 ELEMENTS. (2,500°C POCO Filler Firing Temperature; ITX-ACN Binder; Gas Impregnated)

Thermal stress and other physical property data are listed in Table 6. As noted in Figure 22, the flexural strength and density are linearly related. These data were obtained on the elements fired to 2,200°C (Type 1) prior to impregnations. Flexural strengths of more than 9,000 psi at densities near 1.90 gms/cc appear feasible. Type 2 elements were not tested in flexure. It is probable that these matrix strengths would have been equal to or greater than the strength values obtained on the 2,200°C fired pieces.

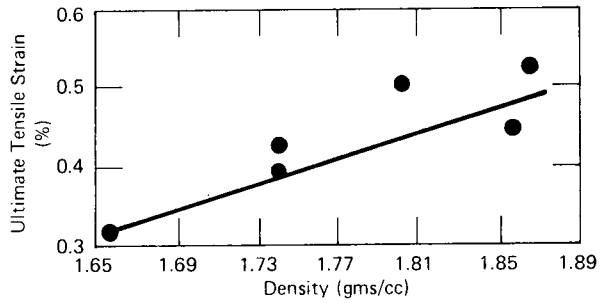


Figure 17. TENSILE STRAIN AS A FUNCTION OF THE DENSITY FOR EXTRUSION 665 ELEMENTS. (2,500°C POCO Filler Firing Temperature; ITX-ACN Binder; Gas Impregnated)

Figure 23 is a graph of the thermal stress resistance of element wafers plotted as a function of density. These data show that the Type 1 matrices were less resistant to thermal stress than the Type 2 elements. Thermal stress resistances significantly increased with bulk density. For comparative purposes, 19-hole element wafers were machined in the with-grain direction from a block of Grade ATJS graphite.[b] Grade ATJS graphite is considered to have excellent thermal stress properties, and also exhibits a low coefficient of thermal expansion. As noted in Figure 22, the ATJS data appear to fit the 850°C bake element data. These data show that very high thermal stress values can be obtained on elements which possess a high coefficient of thermal expansion. When the high CTE matrices are densified to satisfactory densities (1.85 gms/cc), thermal stress resistance values in excess of 1,800 watts are expected. These levels would be an improvement of about a factor of five or more compared to the Pewee 2 element type.

(b) Union Carbide Corporation—Carbon Products Division.

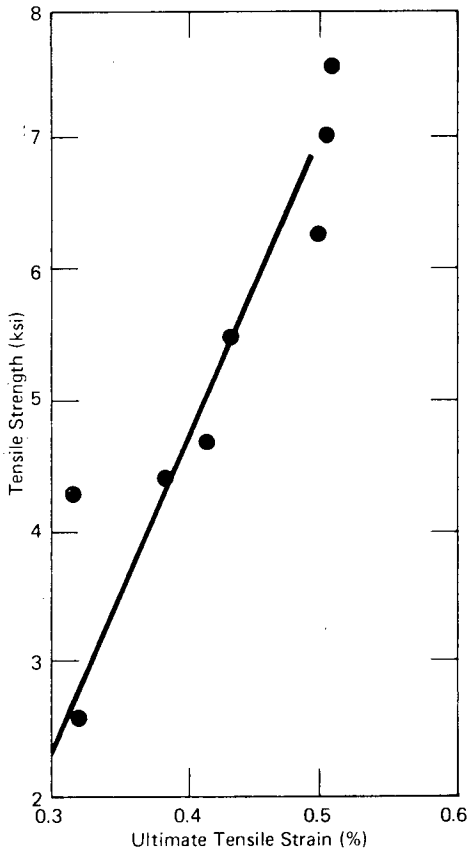


Figure 18. TENSILE STRENGTH AND TENSILE STRAIN OF EXTRUSION 665 ELEMENTS.

Figure 24 relates thermal stress resistances and flexural strengths on Type 1 elements. These data show that thermal stress resistance and flexural strength are closely related. Similar data for Type 2 elements which were impregnated in the 850°C bake state are not available.

Tensile and Tensile Strain to Failure of Impregnated SMC Matrices - In addition to the thermal stress resistance, impregnated elements were tested in tensile by the ORNL and were also measured for tensile strain. The available data are given in Table 7. These data show that gaseous impregnation increases the density, tensile strength, and ultimate strain. The matrices used for this series were SMC (1,000°C) fired filler, bound with the ITX-ACN mixture, and did not contain Thermax. Extrusions 658 and 659 were the same lots which exhibited the high thermal stress resistance.

Isotruxene Elements - A group of nonfueled elements were made using ITX carbon prefired to various temperatures.[7] The elements were pulse-vacuum impregnated using various times to establish a weight gain per unit time. This matrix was not considered to be a prime candidate for the NERVA reactor because the CTE value of the fuel element was less than desired. The available data on three element types are summarized in Table 8. Graphically, a typical impregnation rate curve is as shown in Figure 25. These data show that this type of matrix continues to be densified in a nearly linear rate up to about 52 hours.

Metallographic data at each density level were not taken. At the final density level, no evidence of surface sealing was apparent.

Preproduction Impregnation - Since the production equipment was not available at this time, preproduction uranium-loaded element matrices were routinely impregnated in the development equipment.[7] Matrices of Santa Maria coke, in the 850°C and graphitized state, and primary POCO PCD-0Q matrices were processed. Complete tabulations of the impregnated elements and the carbon pickups are provided in Tables 9 through

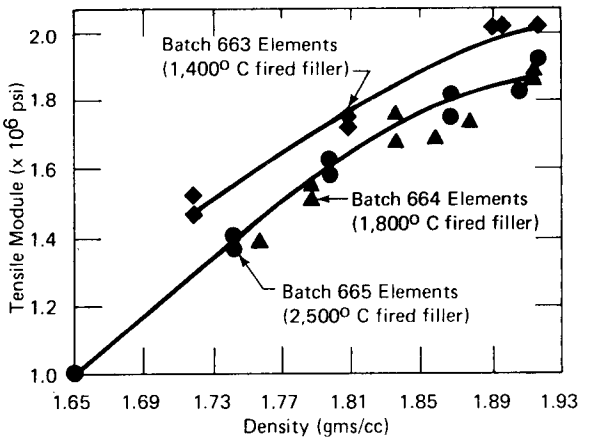


Figure 19. TENSILE MODULUS AS A FUNCTION OF THE DENSITY FOR PRIMARY POCO ELEMENTS.

12. A few of the early runs, noted in Table 10, were made at temperatures up to 760°C. However, the majority of runs were made at 720°C and a cycle of 0.5 second to 2 psig pressure and 4.5 seconds to 27 inches of mercury vacuum. Run times were varied from 24 to 34 hours; the rate per hour was varied depending on the element starting density. Satisfactory densities were obtained using a run time of about 29 hours on any element matrix. No significant problems were observed in impregnating these matrices. In general, all element matrices, regardless of the starting density, had a nearly constant bulk density after impregnation.

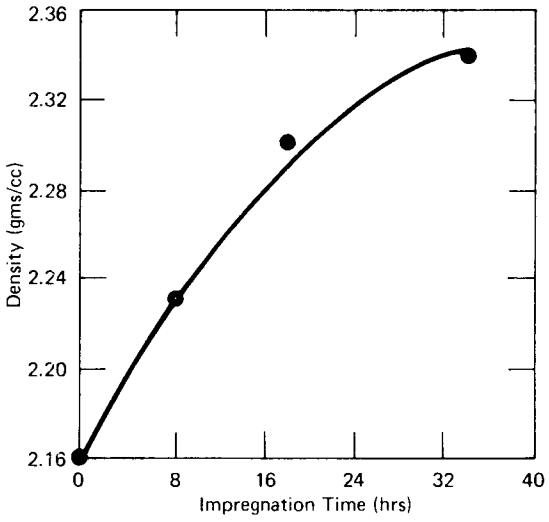


Figure 20. TYPICAL IMPREGNATION RATE OF A GRAPHITIZED SANTA MARIA COKE ELEMENT. (The Rate is a Function of the Initial Density of the Element; ~ 570 mgs U/cc; Element 630-300092)

Butadiene Carbon - During impregnation runs, large quantities of pitch-like materials were formed by the polymerization and decomposition of butadiene.[13] The material was trapped in the piping leading from the bottom of the furnace (< 700°C) and in the cooler portions of the furnace assembly. The pitches had a wide range of softening points, depending on the temperature at which they were formed. In addition, hard carbon deposits were formed at or near the gas inlet point to the furnace (~ 700°C). Two pitches were collected from two temperature points in the outlet lines, and a carbon deposit was taken from the 700°C section of the furnace. The pitches and carbon were heat treated up to 2,800°C. Metallographs of the carbon structure obtained when heat treated to 2,800°C are presented in Figure 26.

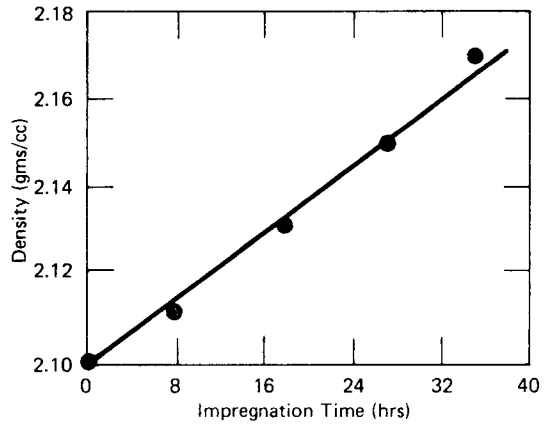


Figure 21. TYPICAL IMPREGNATION RATE OF AN 850°C BAKE SANTA MARIA COKE ELEMENT. (The Rate is a Function of the Initial Density of the Element, the Bulk Density will Increase when Graphitized; ~ 570 mgs U/cc; Element 630-300027)

X-ray data and microstructures show that both pitches formed graphitic, anisotropic carbons with characteristic flow patterns. Carbon deposits from the furnace (~ 700°C) were less graphitic and had some of the characteristics of a glassy carbon. The type of carbon deposited in the fuel element matrices or other test pieces was not completely established. Past experience had shown that the type of carbon was influenced by the plating conditions and the matrix that was being densified. The amount of impregnant carbon has been small in comparison to the overall carbon content.

Table 6

THERMAL STRESS RESISTANCE OF IMPREGNATED SANTA MARIA ELEMENTS

Batch	Impregnation Temperature (° C)	Density (gms/cc)	Flexural Strength (psi)	Thermal Stress Range (watts)
		Type 1(1)		
637	As Graphitized	1.68	5,440	660 - 715
637	750	1.78	6,640	683 - 814
637	750	1.81	7,720	1,250 - 1,346
637	750	1.84	8,110	1,470 - 1,560
		Type 2(2)		
659	As Graphitized	1.62	4,190	560 - 570
658	As Graphitized	1.72	5,670	750 - 760
659	750	1.73	-	1,240 - 1,350
658	700	1.78	-	1,560 - 1,670
		Commercial ATJS(3)		
-	As Received	1.81	-	1,750 - 1,960

(1) Elements graphitized to 2,200° C prior to impregnation.
(2) Elements impregnated after baking to 850° C; impregnant plus element graphitized at 2,200° C.
(3) Fuel element shape; with-grain direction.

Table 7

TENSILE AND TENSILE STRAIN OF IMPREGNATED SANTA MARIA COKE ELEMENTS

Sample	Density (gms/cc) Original	Density (gms/cc) Impregnated	Average Flexural Strength (psi)	Tensile Strength (psi)	Tensile Strain (%)
637	1.68	None	5,440	3,060	0.30
659	1.62	None	4,190	No Data	No Data
658	1.70	None	5,670	No Data	No Data
659	1.64	1.73	-	3,240	0.28
658	1.72	1.78	-	6,060	0.47

All pulse-vacuum studies have used 1,3-butadiene gas as the carbon source.(9) To define the carbon type deposited in the elements, samples of the as-received POCO AXF, as-impregnated POCO AXF, and impregnated, heat-treated POCO AXF have been studied using optical microscopic and electron-beam microscopic techniques. For the optical studies, both as-polished and cathodic-etched samples were studied up to 1,000X. Typical photographs of each of the three specimens are given in Figure 27. Impregnated specimens have fewer voids than nonimpregnated samples. The structural type of the carbon impregnant could not be resolved using optical techniques.

Both as-polished and cathodic-etched samples of each of the three samples were examined using electron microscopic techniques. Typical photographs made at 14,000X of the cathodic-etched samples are presented in Figure 28. The as-received sample had voids which had smooth sides with no definitive structure; the as-impregnated sample had a loosely bonded carbon in the void. No significant structure was apparent.

All impregnated samples were heat treated to 2,800°C. The cathodic-etched samples showed an onionskin-type deposit in the void regions which appeared to be an ordered graphite and was significantly different from the adjoining matrix.

Matrix Evaluation - Several techniques were used to study the matrix structure after impregnation.(6) Potential drop measurements (PDE) indicated that even though sealing occurs, the matrices were filled uniformly in the longitudinal direction. However, this technique could not measure the uniformity in the transverse direction.

Matrices impregnated from a density of 1.70 gms/cc to 1.81 gms/cc have been measured for pore spectrum using mercury porosimetry techniques. The pore spectrum data of Figure 29 are from a nonfueled SMC element bound with ITX, before and after impregnation. Any surface sealing would not be apparent because the surfaces were machined after impregnation. These data show that the open porosity decreased from 20 to 10 percent, while the number of pores less than 0.1 micrometer increased from 18 to 39 percent. However, the overall geometric density changed from 2.09 to 2.01 gms/cc, indicating that a trace of closed porosity was obtained or the carbon impregnant was of low density.

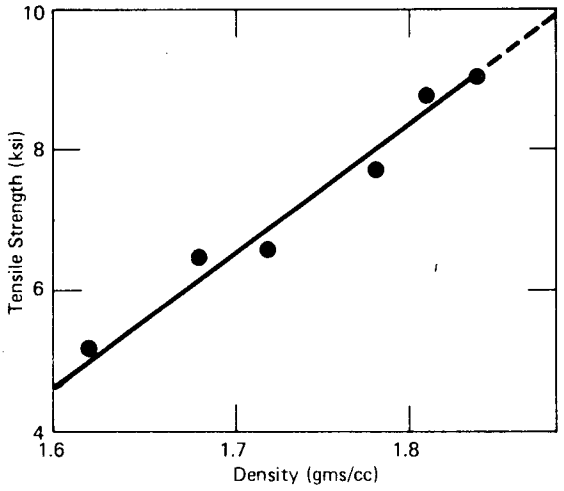


Figure 22. TENSILE STRENGTH AS A FUNCTION OF THE DENSITY. (Type 1 Elements Impregnated after a 2,200°C Bake, then the Element and Impregnant Heated to 2,200°C)

Microstructural changes which normally occurred as a result of impregnation can be seen in Figure 30. These photographs were selected to show a void area in an endeavor to study the impregnation. Specimens were taken from the same elements before and after impregnation. "Before" samples were not the same sample as the "after" ones. The GL 1008 element had most of the small open pores filled with carbon. A thin carbon film can be seen around the larger cavity shown. The SMC element matrix had most of the small holes sealed. Both elements could have been further densified if desired.

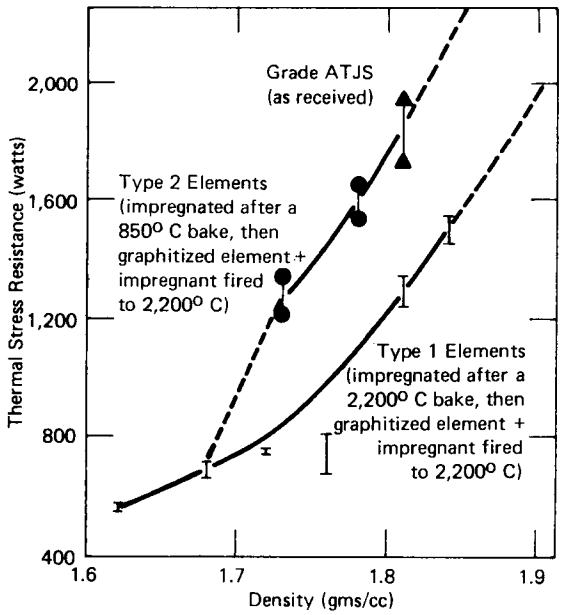


Figure 23. THERMAL STRESS RESISTANCE AS A FUNCTION OF THE DENSITY FOR VARIOUS TYPES OF SANTA MARIA COKE ELEMENTS.

Liquid Impregnation - Experimental graphites were molded and impregnated to produce specimens having nominal dimensions of 2.5 inches long and 3 inches in diameter.[14] These bodies employed several filler carbons and binders and were compounded to obtain physical property data. Low-fired carbons used as fillers included PCD-0Q, GL 1076, ITX, and two types of CAI coke. Binders employed included ITX, CAI, and Grade 350 coal-tar pitch.[8] The physical properties on both the as-made and impregnated graphites were determined.

Different types of experimental graphites were liquid impregnated with a polymer of CAI prepared from CAI which contained less than 500 ppm of potassium. This polymer

produced a well-graphitized "soft" carbon structure. The polymer, made by pressure heating CAI at 300°C and 300 to 800 psi for two to six hours, had a softening point at about 55°C and produced a 50 to 55 percent carbon yield when heated in an open boat to 2,200°C.

The experimental graphites were prepared by mixing a filler and binder and molding the mixture at 1,400°C and 1,600 psi. The pieces were generally heat treated up to 2,800°C without pressure prior to impregnation. However, a limited amount of work was directed toward impregnating the 1,400°C baked graphites. The experimental fillers ranged from isotropic to anisotropic carbons. In almost all cases, the filler firing temperature was 1,000°C. The binders used were thermoplastic types and included ITX, CAI polymer, and 350 coal-tar pitch.

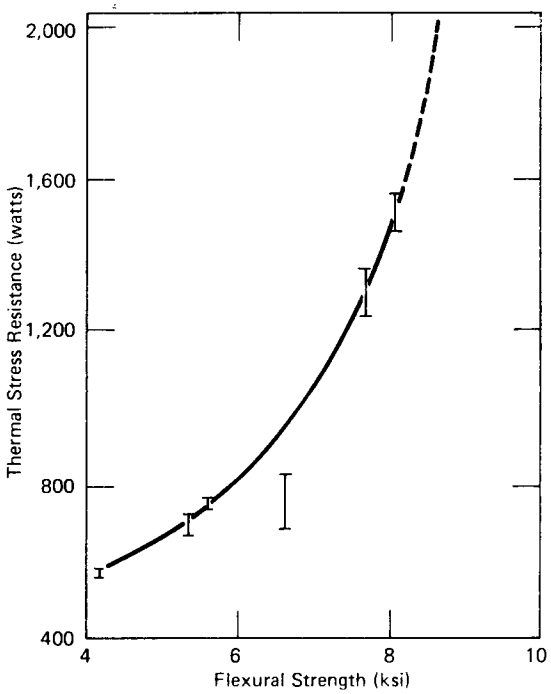
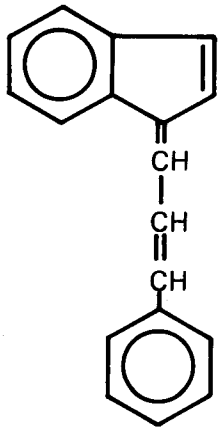


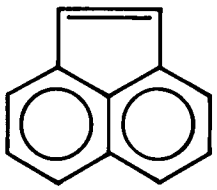
Figure 24. FLEXURAL STRENGTH VERSUS THERMAL STRESS RESISTANCE FOR TYPE 1 ELEMENTS.

Cinnamylideneindene - Recent developments associated with reactor and aerospace technology have placed emphasis on strong, low-density materials such as carbon. Thus, there is a renewed interest in carbon; and, particularly, in those factors which influence its properties. Since property changes associated with polymerization sequences are known to have a pronounced effect on the properties of a derived carbon, this study was an effort to gain understanding of the high-temperature polymerization of a carbon precursor and to establish a correlation between the properties of the polymer and those of the derived carbon.

One precursor material chosen for study was cinnamylideneindene (CAI):[15]



which can be prepared by the room-temperature reaction of indene with cinnamaldehyde in a methanol-potassium hydroxide solution.[15] Molecular weight distributions of typical produced CAI are shown by the gel permeation chromatographic (GPC) scans in Figure 31. Acenaphthalene (ACN):



polymerization has previously received attention in the literature[16 - 18] and was included in this study so that analogies and contrasts could be made with the experimental data obtained for CAI.

Table 8

MULTIPLE IMPREGNATION OF EXPERIMENTAL SECOND BAKE ISOTRUXENE ELEMENTS

		Element Numbers[1]											
		000-666-03[2]				000-667-03[3]				000-668-03[4]			
Temperature (°C)	Total Time (hrs)	Increase in Weight (gms)		Increase in Density (gm/cc)		Increase in Weight (gms)		Increase in Density (gm/cc)		Increase in Weight (gms)		Increase in Density (gm/cc)	
		Δ	Total	Δ	Total	Δ	Total	Δ	Total	Δ	Total	Δ	Total
730	8	4.6	4.6	0.01	0.01	5.9	5.9	0.02	0.02	7.4	7.4	0.02	0.02
730	18	11.6	16.2	0.03	0.04	10.9	16.8	0.02	0.04	15.4	22.8	0.04	0.06
730	27	7.7	23.9	0.02	0.06	6.9	23.7	0.02	0.06	12.7	35.5	0.03	0.09
720	35	5.8	29.7	0.02	0.08	5.1	28.8	0.01	0.07	6.3	41.8	0.02	0.11
720	45	2.5	32.2	0.01	0.09	2.6	31.4	0.01	0.08	2.0	43.8	0.01	0.12
720	69	6.5	38.7	0.02	0.11	6.3	37.7	0.02	0.10	10.7	54.5	0.03	0.15
Final Density (gms/cc)			1.70				1.69				1.77		

(1) The elements or impregnant had not been graphitized. In general, a nominal density increase of 0.15 gm/cc occurred because of this operation.
(2) Carbon fired at 900° C.
(3) Carbon fired at 1,000° C.
(4) Carbon fired at 1,500° C.

Low-Temperature Polymerization - Since polymeric forms of both CAI and ACN were used, a brief look at the low-temperature polymerization properties of these two materials was desirable.

Structures of both CAI and ACN incorporate unsaturated bonding with a high degree of conjugation; which, in turn, enhances their reactivities toward polymerization. Both ACN (mp, 88°C) and CAI (mp, 190°C) polymerize at temperatures just above that required for melting and both have similar polymerization sequences in that they initially react to give linear, high-molecular-weight polymers which tend to degrade at higher temperatures. Lower-molecular-weight fragments tend to form cyclic or condensed structures.

Differential thermal analysis (DTA) scans, given in Figures 32 and 33, indicate a significant polymerization exotherm immediately succeeding the exotherm associated with fusion. During this initial polymerization, the molecular weight increases from 230 for the CAI monomer to approximately 900 (Table 13). This initial polymer degrades from a molecular weight of approximately 900 to a molecular weight of approximately 500 at temperatures above 200°C. The DTA scan with CAI (Figure 32) shows a second exotherm at 280 - 380°C, probably representing cyclization or rearrangement reactions. At 390°C,

Table 9

IMPREGNATION OF SECOND BAKE URANIUM LOADED POCO PRODUCTION ELEMENTS

Element Number	Run Number	Temperature (° C)	Time (hrs)	Weight (gms)		Density[1] (gms/cc)		
				Before	Δ	Before	After	Δ
500-300-149[2]	9	730	24	710	30	1.92	2.00	0.08
-150[2]	9	730	24	707	33	1.91	2.00	0.09
-155[2]	9	730	24	709	32	1.92	2.01	0.09
-157[2]	9	730	24	710	29	1.93	2.01	0.08
-153[3]	10	730	24	615	23	1.91	1.98	0.07
-153[3]	12	720	17	638	9	1.98	2.00	0.02
-156[3]	10	730	24	621	23	1.92	2.00	0.08
-156[3]	12	720	17	645	8	2.00	2.02	0.02
-160[4,5]	17	720	29	708	28	2.12	2.20	0.08
-163[4,5]	17	720	29	722	29	2.11	2.19	0.08
-164[4,6]	17	720	29	731	27	2.07	2.15	0.08
-165[4,6]	17	720	29	735	27	2.02	2.10	0.08
-166[4,6]	17	720	29	719	27	2.04	2.12	0.08
-168[4,5]	17	720	29	717	24	2.03	2.10	0.07
-169[4,5]	17	720	29	717	26	2.09	2.16	0.07
-170[4,5]	17	720	29	705	26	2.10	2.17	0.07
-171[4,6]	17	720	29	714	26	2.05	2.12	0.07
-303[4]	20	720	22	720	20	2.04	2.10	0.06
-314[4]	20	720	22	741	18	2.11	2.16	0.05
-316[4]	20	720	22	748	19	2.13	2.19	0.06
-323[4]	20	720	22	724	18	2.05	2.10	0.05
-326[4]	20	720	22	716	21	2.00	2.06	0.06
-332[4]	20	720	22	726	16	2.05	2.10	0.05
-333[4]	20	720	22	713	16	2.02	2.07	0.05
-336[4]	20	720	22	726	18	2.10	2.15	0.05
-340[4]	20	720	22	736	18	2.11	2.16	0.05
-344[4]	20	720	22	726	18	2.10	2.15	0.05
-303[4]	21	720	8	739	4.3	2.10	2.11	0.01
-314[4]	21	720	8	760	3.0	2.16	2.17	0.01
-316[4]	21	720	8	767	4.2	2.19	2.20	0.01
-323[4]	21	720	8	742	4.8	2.10	2.11	0.01
-326[4]	21	720	8	737	6.4	2.06	2.08	0.02
-332[4]	21	720	8	742	4.6	2.10	2.11	0.01
-333[4]	21	720	8	729	4.3	2.07	2.08	0.01
-336[4]	21	720	8	744	3.9	2.15	2.16	0.01
-340[4]	21	720	8	755	4.2	2.16	2.17	0.01
-344[4]	21	720	8	744	4.3	2.15	2.16	0.01

(1) Bulk densities were increased when graphitized.
(2) Outside diameter, 0.801 inch; bore, 0.120 inch; length, 56 inches.
(3) Machined to 0.767 inch outside diameter, 0.103 inch bore, and 56 inches long.
(4) Nominally a 0.785 inch outside diameter, 0.100 inch bore, and 54 to 56 inches long.
(5) Leached with HCl at 1,500° C.
(6) Leached with Cl_2 at 1,300° C.

weight loss becomes significant and continues at a relatively constant rate to approximately 550°C. The DTA scan for ACN (Figure 33) shows a polymerization exotherm beginning at approximately 100°C and becoming quite intense at approximately 190°C. Apparently, degradation of polymeric ACN is significant over the temperature range from 350 to 425°C, as suggested by the endotherm in Figure 33. Muller[18] has represented the polymerization of acenaphthalene with the mechanism shown in Figure 34. His mechanism, as well as the one originally proposed by Ruland,[16] supports the contention that the formation of a linear polymer of ACN occurs first. This action is followed by degradation and then the formation of condensed or cyclic structures.

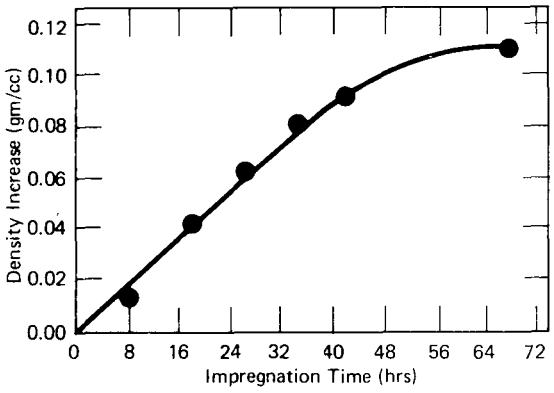
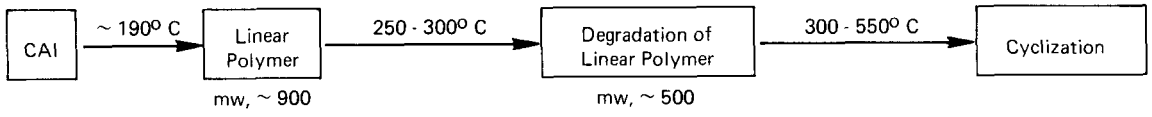
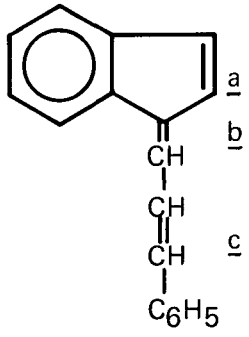


Figure 25. TYPICAL IMPREGNATION RATE OF AN ISOTRUXENE CARBON ELEMENT. (Element 000-666-03; Carbon Prefired to 900°C)

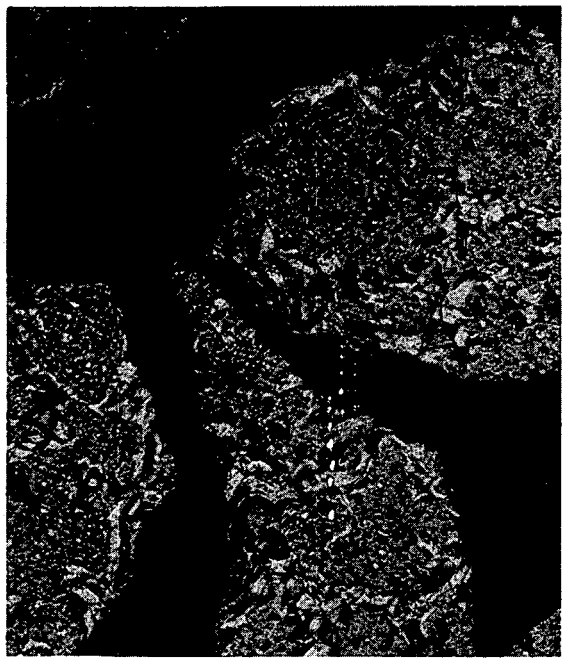
Polymerization mechanisms for CAI are probably more complex due to the presence of more than one reactive site per molecule. However, DTA and molecular weight data are consistent with the following generalizations:



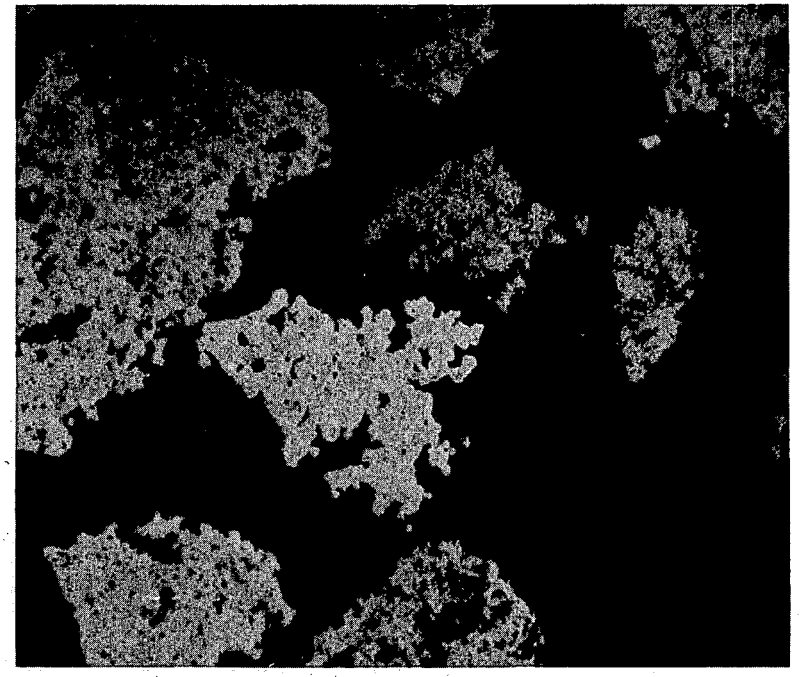
Although the exact polymerization mechanism is unknown, reactive sites are apparent. There are three possible bonds at which 1,2-type polymerization might be expected, designated as a, b, and c in the CAI structure:



(a) Pitch Softening Point ~ 30°C.

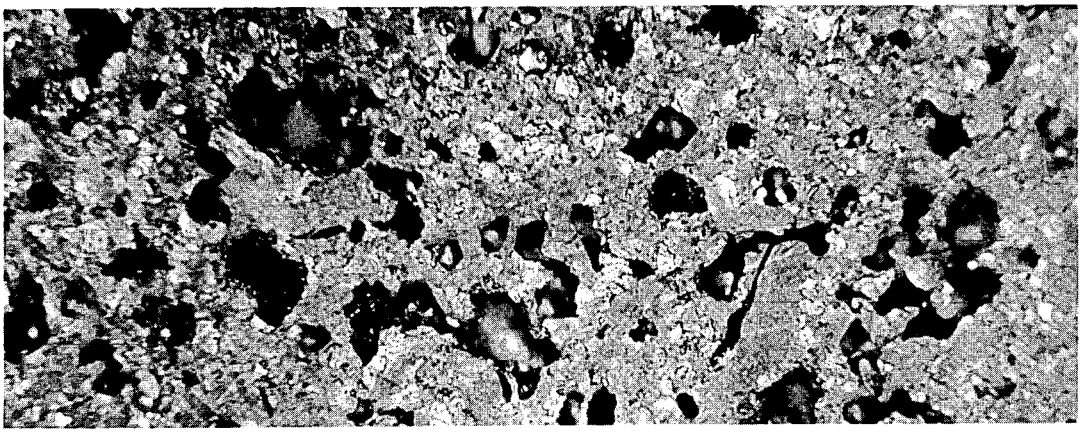


(b) Pitch Softening Point ~ 60°C.

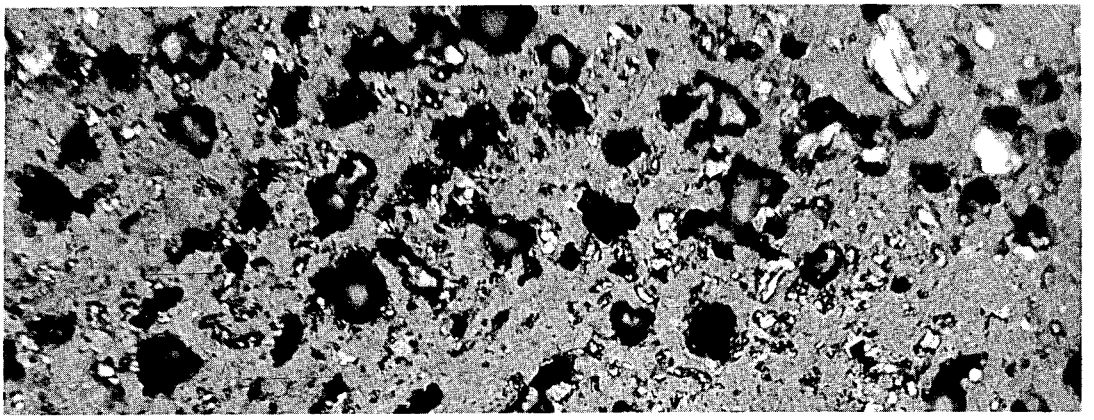


(c) Carbon from the ~ 600°C Zone of the Furnace.

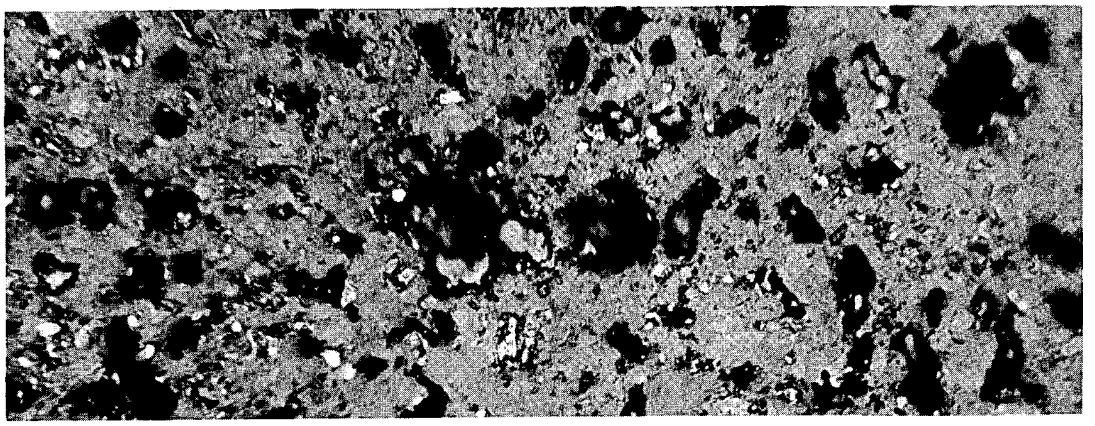
Figure 26. CARBONS OBTAINED FROM BUTADIENE. (Carbons Fired to 2,800°C; Sensitive Tint; 250X)



(a) As Received. H246-1b



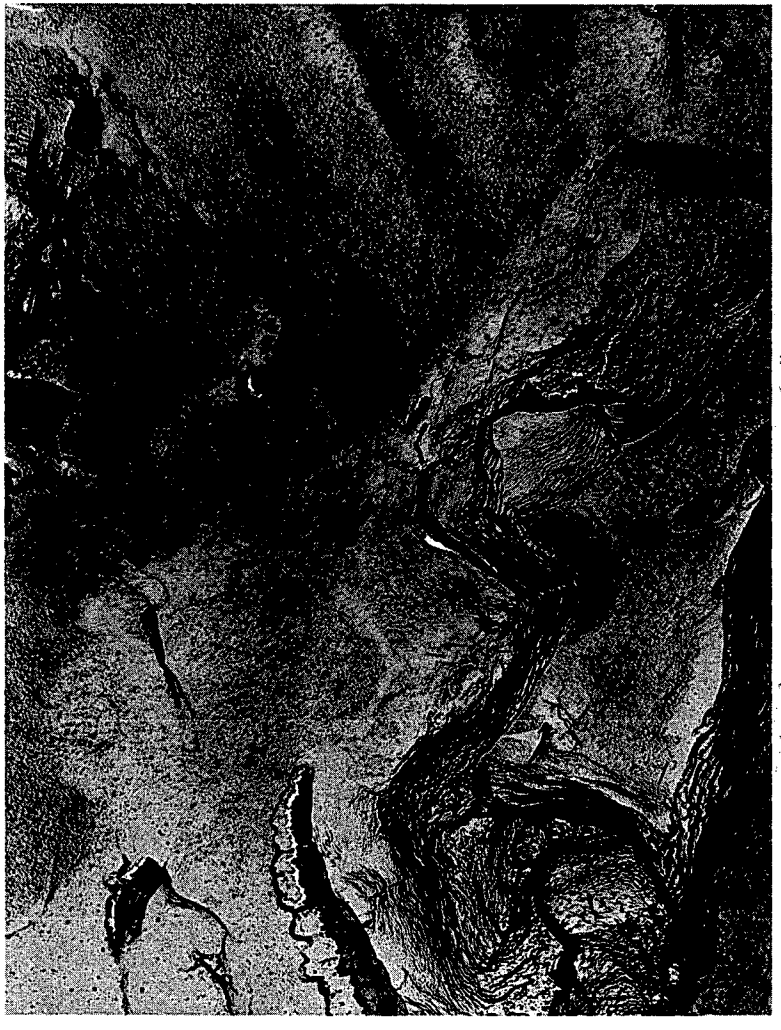
(b) As Impregnated. H246-2c



(c) Impregnated, then Heat Treated to 2,800°C. H246-3c

Figure 27. METALLOGRAPHS OF POCO AXF GRAPHITE. (1,000X)

(a) POCO AXF, Cathodically Etched. EM-6500



(b) Impregnated and Heat Treated POCO AXF, Cathodically Etched. EM-6470

Figure 28. ELECTRON MICROSCOPE PHOTOGRAPHS OF POCO AXF GRAPHITE. (14,000X)

Table 10

IMPREGNATION OF URANIUM LOADED SECOND-BAKE SANTA MARIA COKE PRODUCTION ELEMENTS AT VARIOUS TEMPERATURES

Element Number[2]	Run Number	Temperature (°C)	Time (hrs)	Weight (gms)		Density[1] (gms/cc)		
				Before	Δ	Before	After	Δ
630-300-025[3]	3	740	24	783	27	2.09	2.16	0.07
-031[3]	3	740	24	787	20	2.10	2.15	0.05
-037	3	740	24	827	20	2.16	2.21	0.05
-043[3]	3	740	24	771	49	2.06	2.19	0.13
-045	3	740	24	829	20	2.16	2.22	0.06
-055	3	740	24	794	62	2.06	2.23	0.17
-057	3	740	24	827	16	2.16	2.20	0.04
-063[3]	3	740	24	803	19	2.14	2.19	0.05
-067[3]	3	740	24	760	63	2.03	2.19	0.16
-069	3	740	24	836	24	2.17	2.23	0.06
-029	5	760	21	774	13	2.05	2.09	0.04
-033	5	760	21	777	39	2.06	2.16	0.10
-041[3]	5	760	21	761	35	2.03	2.12	0.09
-065	5	760	21	785	23	2.08	2.14	0.06
-077[3]	5	760	21	763	34	2.03	2.12	0.09
-079	5	760	21	750	68	1.99	2.17	0.18
-036	9	730	24	756	27	2.05	2.12	0.07
-038	9	730	24	755	35	2.06	2.15	0.09
-040	9	730	24	754	32	2.06	2.14	0.08
-042	9	730	24	755	33	2.06	2.14	0.08
-044	9	730	24	757	32	2.06	2.14	0.08
-117[4]	10	730	24	697	13	2.16	2.19	0.03
-123[4]	10	730	24	695	14	2.15	2.19	0.04
-125[4]	10	730	24	680	29	2.11	2.19	0.08
-133[4]	10	730	24	701	13	2.17	2.21	0.04
-141[4]	10	730	24	668	25	2.07	2.15	0.08
-143[4]	10	730	24	670	24	2.07	2.15	0.08
-145[4]	10	730	24	672	24	2.08	2.16	0.08
-146[4]	10	730	24	672	24	2.08	2.16	0.08

(1) Bulk densities were increased when graphitized.
(2) Elements were nominally 0.800 inch outside diameter, 0.102 inch bore, and 56 to 59 inches long.
(3) Skinned.
(4) Machined to 0.767 inch outside diameter, 0.103 inch bore, and 56 inches long.

The bonding in b would probably be less reactive to polymerization than a or c, due to steric hindrance. Polymerization by a would be somewhat analogous to that in ACN. There are two possible ways for 1,4-type polymerization: bonding through a and b or through b and c. Such a mechanism could produce linear or cyclic polymers, the latter via Diels-Alder-type reactions. In addition, polymerization could also involve bonding through a and c in a 1,6 manner.

Efforts to determine the exact mechanism of CAI polymerization were attempted with emphasis concentrating on applications of NMR spectroscopy. However, hydrogen signals associated with the various types of olefinic bonds were difficult to distinguish and the results were inconclusive.

Four different samples of polymeric CAI were prepared by heating the CAI in an autoclave for two hours at four different temperatures (200, 250, 300, and 340°C). (Further reference to a specific CAI polymer will be made using notations such as CAI-200 and

Table 11

IMPREGNATION OF URANIUM LOADED SECOND-BAKE SANTA MARIA COKE PRODUCTION ELEMENTS AT 720° C

Element Number(2)	Run Number	Time (hrs)	Weight (gms)		Density(1) (gms/cc)		
			Before	Δ	Before	After	Δ
630-300-087	15, 16	34	790	37	2.09	2.19	0.10
-089	15, 16	34	795	33	2.11	2.19	0.08
-093	15, 16	34	795	41	2.11	2.21	0.10
-095	15, 16	34	789	44	2.09	2.20	0.11
-097	15, 16	34	791	37	2.09	2.19	0.10
-101	15, 16	34	791	39	2.09	2.19	0.10
-103	15	10	789	19	2.09	2.14	0.05
-103	16	24	808	23	2.14	2.20	0.06
-105	15	10	788	18	2.09	2.14	0.05
-105	16	24	806	25	2.14	2.20	0.06
-107	15, 16	34	791	39	2.09	2.19	0.10
-109	15	10	788	14	2.09	2.13	0.04
-109	16	24	802	24	2.13	2.19	0.06
-035	18	28	800	13	2.14	2.18	0.04
-071	18	28	771	60	2.01	2.17	0.16
-073	18	28	770	64	2.03	2.19	0.16
-081	18	28	781	53	2.04	2.18	0.14
-083	18	28	799	31	2.09	2.17	0.08
-111	18	28	792	31	2.07	2.15	0.08
-113	18	28	792	34	2.07	2.16	0.09
-115	18	28	793	31	2.07	2.15	0.08

(1) Bulk densities were increased when graphitized.
(2) Elements were nominally 0.800 inch outside diameter, 0.102 inch bore, and 56 to 59 inches long.

CAI-250 to denote the polymerization temperature of the materials used in the study; the CAI monomer will be denoted by CAI-M.) Molecular-weight distributions for the autoclave-produced CAI polymers are portrayed in Figure 35. The polyacenaphthalene was prepared by heating ACN in an open reactor for approximately 14 hours. GPC scans of the ACN starting material and the resulting polymer can be seen in Figure 36. The maximum molecular size of the GPC standard (sucrose octacetate) was 48,000 A.

Preparation of Cinnamylideneindene - CAI preparation involved the condensation of indene and cinnamaldehyde in the presence of potassium hydroxide.

A solution of 264 grams (2 moles) of cinnamaldehyde in 250 milliliters of methanol was added dropwise over two hours in a stirred solution of 348 grams (3 moles) of indene and 80 grams (2 moles) of potassium hydroxide in 2 liters of methanol.[19] After one hour, the precipitated CAI was collected by filtration and dried at 60°C for 12 hours (mp, 190 - 191°C).

It has also been determined that the carbon derived from CAI containing the potassium impurity can be significantly affected by this impurity. To determine if potassium was a specific agent in the CAI production, other base salts were evaluated. Included in this test series were sodium hydroxide, lithium hydroxide, sodamide, and triethylamine. All of these base compounds, except triethylamine, did produce CAI in a manner similar to potassium hydroxide. Table 14 lists the CAI product yield and purity for each of the basic materials.

Table 12

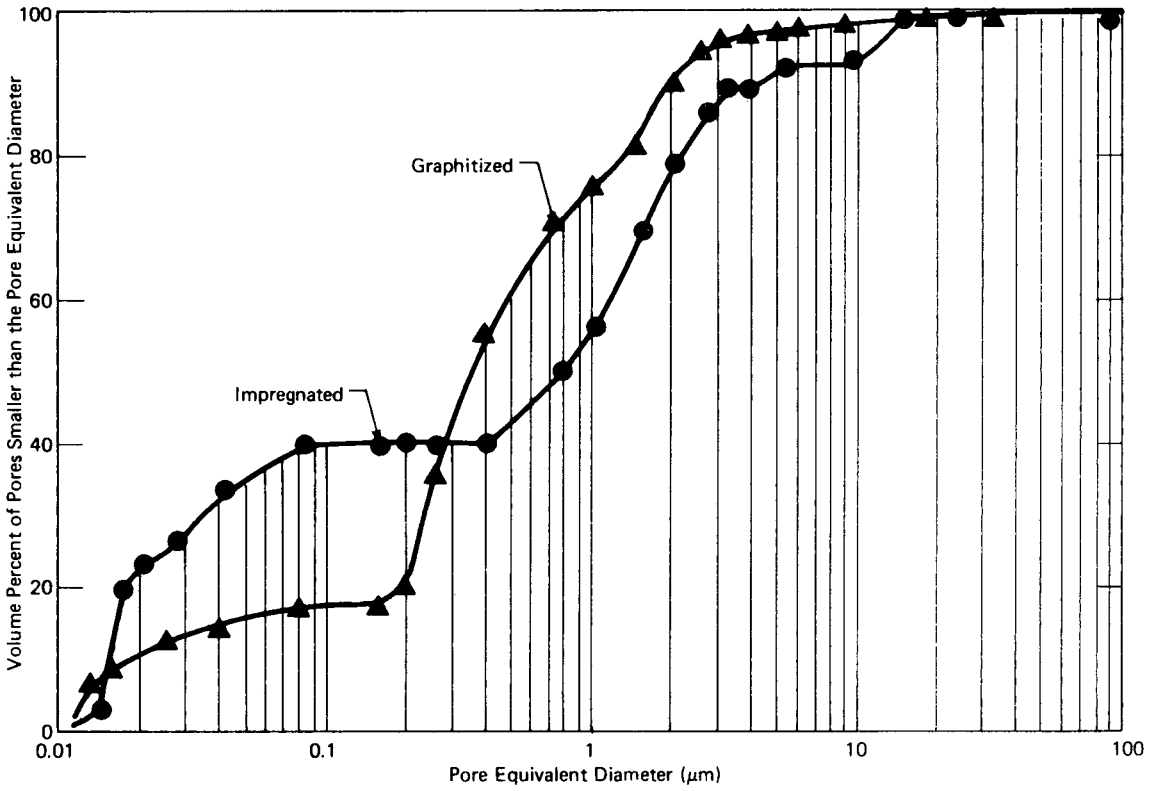
IMPREGNATION OF URANIUM LOADED GRAPHITIZED SANTA MARIA COKE PRODUCTION ELEMENTS

Element Number(1)	Run Number	Temperature (° C)	Time (hrs)	Weight (gms)		Density (gms/cc)		
				Before	Δ	Before	After	Δ
630-300-026	4	750	24	624	34	2.13	2.25	0.12
-032	4	750	24	636	30	2.17	2.27	0.10
-042	4	750	24	634	31	2.16	2.27	0.11
-054	4	750	24	643	24	2.19	2.27	0.08
-058	4	750	24	632	36	2.16	2.28	0.12
-062	4	750	24	612	51	2.09	2.26	0.17
-068	4	750	24	646	21	2.21	2.28	0.07
-074	4	750	24	639	23	2.18	2.26	0.08
-078	4	750	24	606	56	2.07	2.26	0.19
-086	4	750	24	621	43	2.12	2.27	0.15
-034	11	720	24	646	17	2.20	2.26	0.06
-038	11	720	24	641	13	2.19	2.23	0.04
-050	11	720	24	636	23	2.17	2.25	0.08
-096	11	720	24	623	38	2.13	2.26	0.13
-106	11	720	24	624	38	2.13	2.26	0.13
-108	11	720	24	627	34	2.14	2.26	0.12
-124	11	720	24	641	16	2.19	2.25	0.06
-126	11	720	24	636	16	2.17	2.23	0.06
-128	11	720	24	638	17	2.18	2.24	0.06
-134	11	720	24	645	18	2.20	2.26	0.06
-060	12	720	18	648	20	2.21	2.28	0.07
-102	12	720	18	623	44	2.13	2.28	0.15
-104	12	720	18	622	47	2.13	2.29	0.16
-112	12	720	18	624	41	2.14	2.28	0.14
-114	12	720	18	625	43	2.14	2.29	0.15
-116	12	720	18	623	44	2.13	2.29	0.16
-118	12	720	18	640	24	2.19	2.27	0.08
-122	12	720	18	640	24	2.19	2.27	0.08
-066	8	730	9	640	12	2.19	2.23	0.04
-066	13	720	8	652	5	2.23	2.25	0.02
-066	14	720	10	657	3	2.25	2.26	0.01
-092	7	730	10	628	21	2.16	2.23	0.07
-092	8	730	9	649	18	2.23	2.29	0.06
-092	9	730	24	667	11	2.29	2.33	0.04
-072	13	720	8	635	10	2.17	2.21	0.04
-072	14	720	10	645	5	2.21	2.23	0.02

(1) Elements were machined to 0.752 inch outside diameter, 0.102 inch bore, and 53 1/4 inches long.

Higher product yields resulted from the use of sodium hydroxide, but product purity (with respect to the organic monomer content) seemed essentially independent of the base materials. Thus, the product isolated when using sodium hydroxide was quite similar in yield and purity to that produced when using potassium hydroxide.

Acetic Acid Contamination - When CAI powder was washed with an acetic acid-methanol solution to remove excess potassium salts, excess acetic acid-methanol solution remained in the CAI powder.(7) The excess acid-methanol wash solution was difficult to remove under low-temperature ($< 60^{o}C$) drying conditions. If not removed, the acid-methanol solutions promoted undesirable polymerization of CAI at higher temperatures.



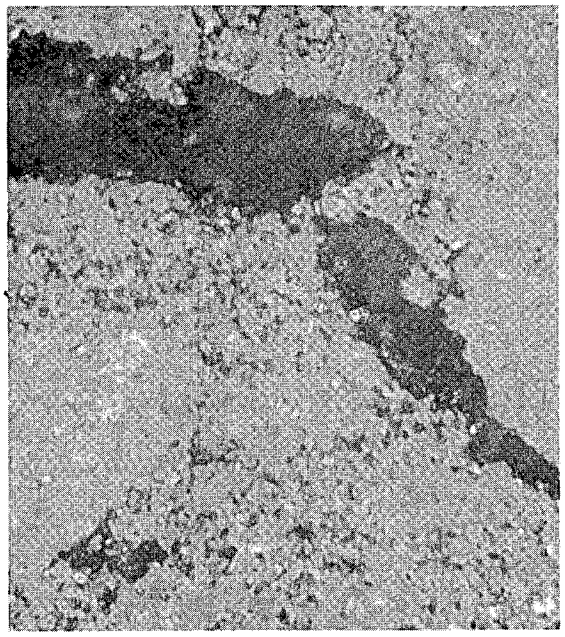
	Graphitized	Impregnated
Bulk Density (gms/cc)	1.675	1.814
Porosity (%)	19.75	9.55
Real Density (gms/cc)	2.09	2.01
Porosity < 10 μm (%)	98.83	93.33
Porosity < 0.1 μm (%)	18	39

Figure 29. EFFECT OF A GAS-PULSE IMPREGNATION OF THE STRUCTURE OF A SANTA MARIA COKE, ISOTRUXENE-BOUND GRAPHITE.

Samples that were moist with acetic acid were initially heated to 60°C in two beakers of different sizes such that one sample was 3.5 inches high by 4.1 inches in diameter while a smaller sample was 2.9 inches high by 2.9 inches in diameter. No polymerization was noted at 60°C. After 12 hours at 80°C, polymerization had occurred in the larger sample. The smaller sample did not polymerize under these conditions but did at 100°C. Thus, the polymerization temperature was somewhat influenced by the sample size which was related to the ability of a sample to dissipate heat. A sample of CAI, moist with acetic acid, was washed in methanol, allowed to dry, and subsequently heated. No polymerization was noted after two days at 100°C. Thus, low-temperature polymerization was promoted by the presence of residual acetic acid and did not tend to occur for acid-free samples.

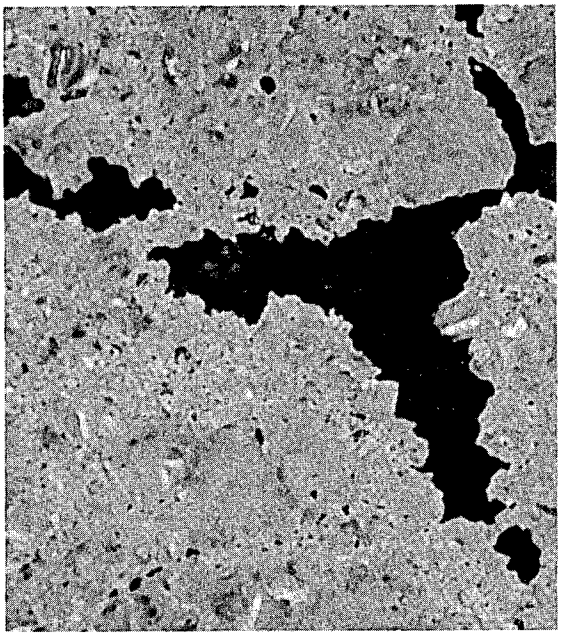
Pressure Polymerization of CAI - Pressure polymerization of CAI could be desirable because the melting point can be reduced and the molecular weight changed. Polymerization reactions were carried out at various autoclave temperatures and for various heat-treatment times. Attempts were made to correlate the polymerization conditions with polymer properties and properties of derived carbons.

(a) As Graphitized GL 1008-ITX-ACN.



(b) As Graphitized SMC-ITX-ACN.

(c) Impregnated GL 1008-ITX-ACN.



(d) Impregnated SMC-ITX-ACN.

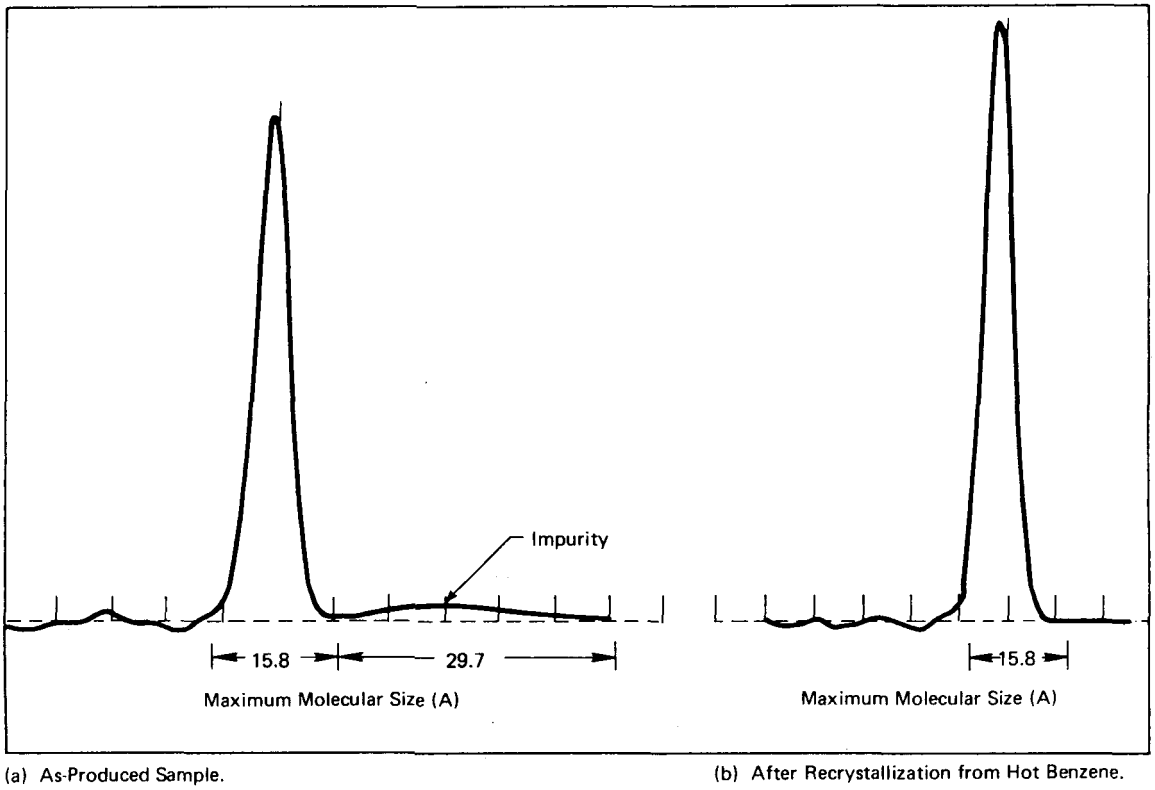
Figure 30. MICROSTRUCTURAL CHANGES AS A RESULT OF GAS IMPREGNATION. (The Large Voids are Areas Selected for Studying the Carbon Impregnant Distribution; 1,000X)

Table 13

MELTING POINT AND AVERAGE MOLECULAR WEIGHT DATA FOR POLYMERS OF CINNAMYLIDENE-INDENE AND ACENAPHTHALENE

Compound	Polymerization Temperature (° C)	Melting Point Range (° C)	Average Molecular Weight(1)
CAI	0	190	230
	200(2)	135 - 150	907
	250(2)	73 - 95	539
	300(2)	60 - 90	504
	340(2)	35 - 40	434
ACN	0	88	152
	300(3)	120 - 130	298

(1) Determined by vapor phase osmometry.
(2) Polymerized in an autoclave by heating for two hours at the indicated temperature.
(3) Polymerized by heating in an open beaker at 300° C for approximately 14 hours.



(a) As-Produced Sample.

(b) After Recrystallization from Hot Benzene.

Figure 31. GEL PERMEATION CHROMATOGRAPHIC SCANS SHOWING THE MOLECULAR DISTRIBUTION OF LABORATORY-PRODUCED CINNAMYLIDENEINDENE.

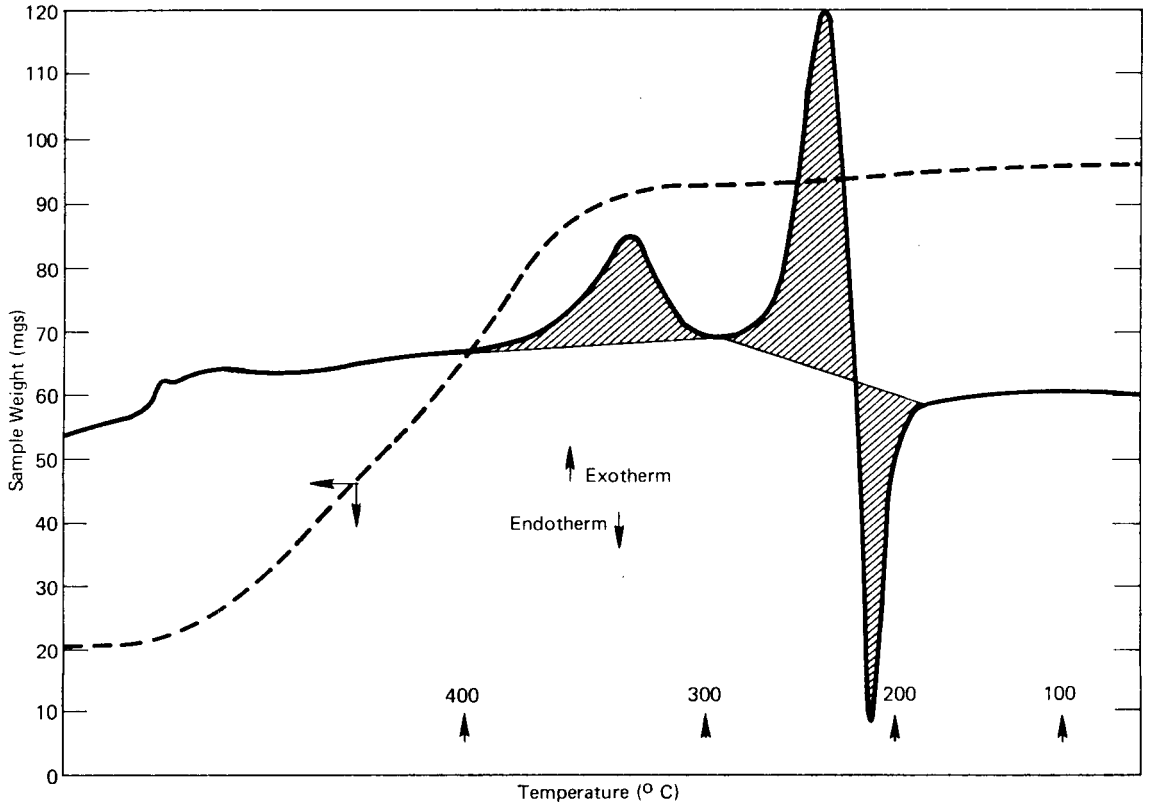


Figure 32. DIFFERENTIAL THERMAL ANALYSIS CURVE FOR CINNAMYLIDENEINDENE. (Heating Rate, 6°C/min)

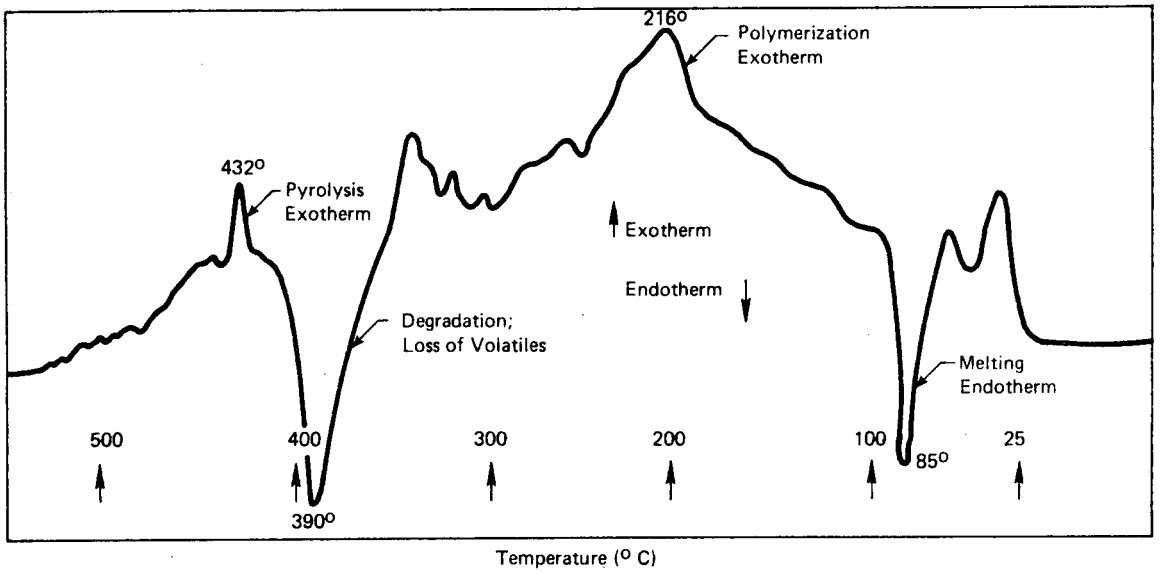


Figure 33. DIFFERENTIAL THERMAL ANALYSIS CURVE FOR ACENAPHTHALENE. (Heating Rate, 6°C/min)

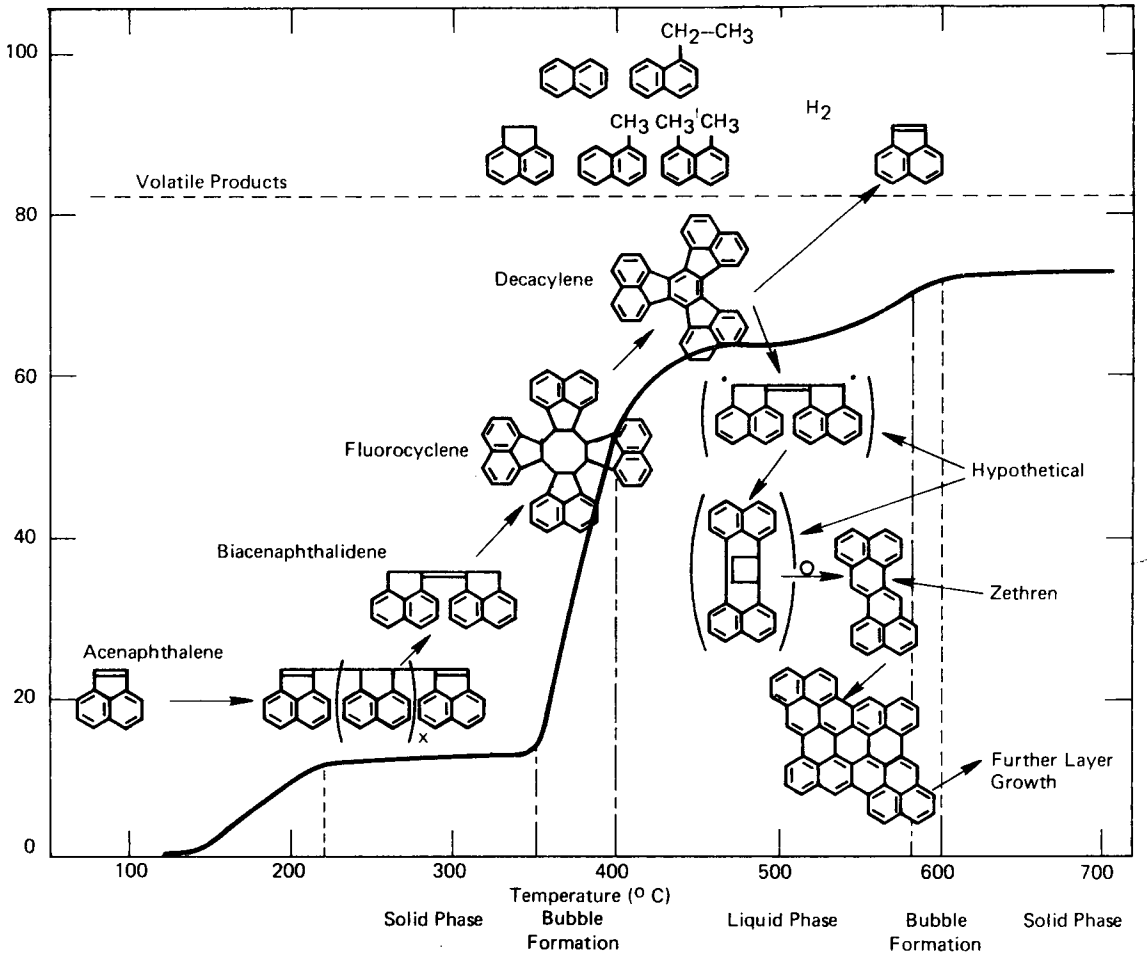


Figure 34. MECHANISM FOR THE CARBONIZATION OF ACENAPHTHALENE.

Table 14

SYNTHESIS OF CINNAMYLIDENEINDENE USING VARIOUS BASIC MATERIALS

Sample Number(1)	Basic Material Used		Yield of CAI Product(2) (%)	Purity of CAI Product(3) (% monomer)
	Type	Quantity (gms)		
H2-43A	NaOH	10	52	90
H2-43B	LiOH	6	39	88
H2-44B	$NaNH_2$	10	44	91
H2-44A	$(C_2H_5)_3N$	17	No CAI Product Isolated	

(1) With the exception of the basic components, all preparatory batches consisted of 58 grams of indene, 380 mils of methanol, and 44 grams of cinnamaldehyde. All reactions were carried out at 30° C.

(2) Calculations based on the quantity of cinnamaldehyde used.

(3) Estimated by GPC analyses.

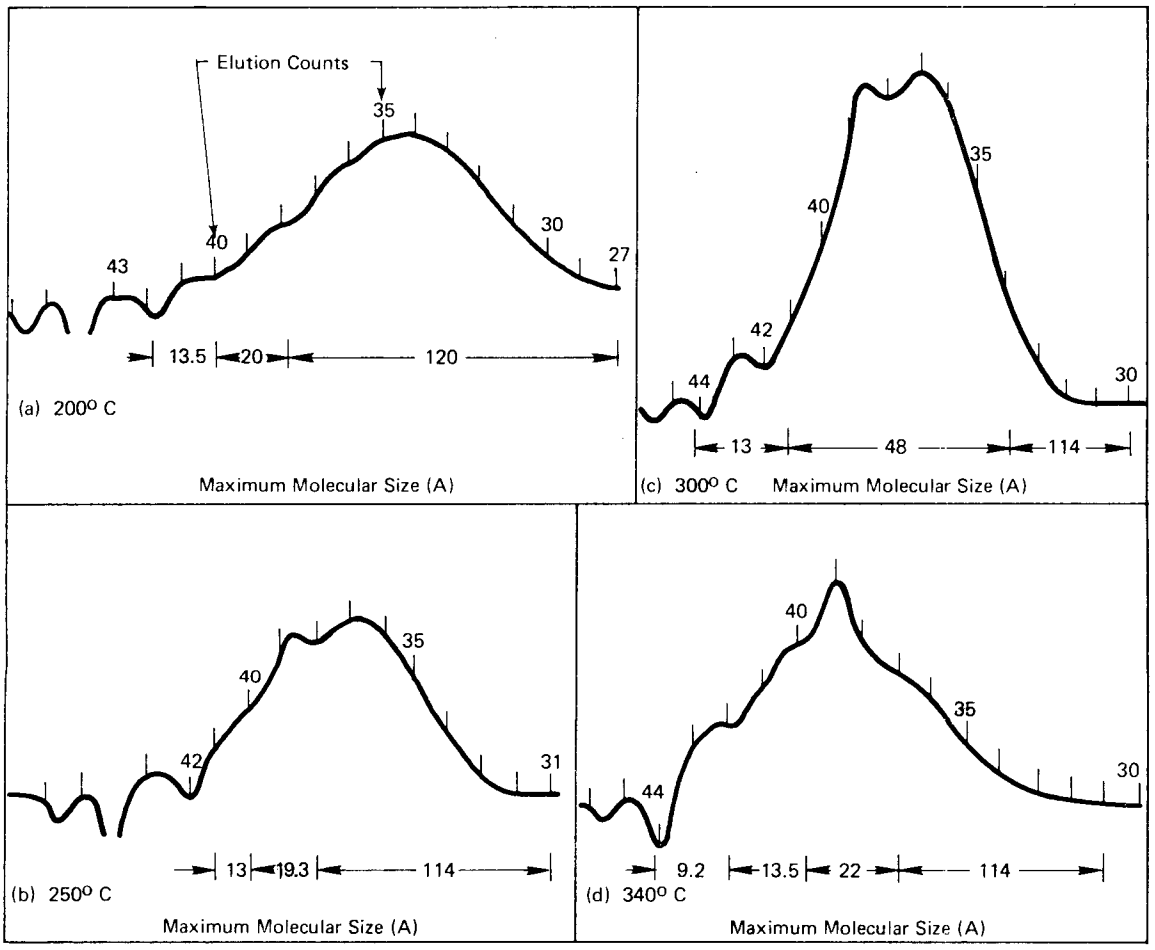


Figure 35. GEL PERMEATION CHROMATOGRAPHIC SCANS SHOWING THE MOLECULAR DISTRIBUTIONS OF CINNAMYLIDENEINDENE POLYMERS PRODUCED BY AUTOCLAVE TREATMENT FOR TWO HOURS AT THE DESIGNATED TEMPERATURE.

Cinnamylideneindene was polymerized by heating for two hours at 200, 250, 300, and 340°C in an autoclave (Figure 37) under an initial (room temperature) nitrogen pressure of 300 psi.(15)

As indicated in Figure 38, melting temperatures of the CAI polymers were a function of the autoclave temperature, with minimum values of 60 to 75°C resulting from a heat treatment at approximately 300°C for six hours. The melting temperature of the CAI monomer is approximately 190°C. As is evident in Figure 38, the melting temperatures of CAI polymerized at 200°C for six hours exceeded that of the monomer.

Corresponding to this decrease in the melting temperature (with increasing autoclave temperatures) is a decrease in the average molecular weight (Figure 39). For six-hour heating periods, minimum values of approximately 380 were observed for the 300°C-polymerized samples. This trend follows that of the melting temperatures previously discussed for six-hour samples. For shorter heating periods, this minimum in the average molecular weight values occurred at higher autoclave temperatures.

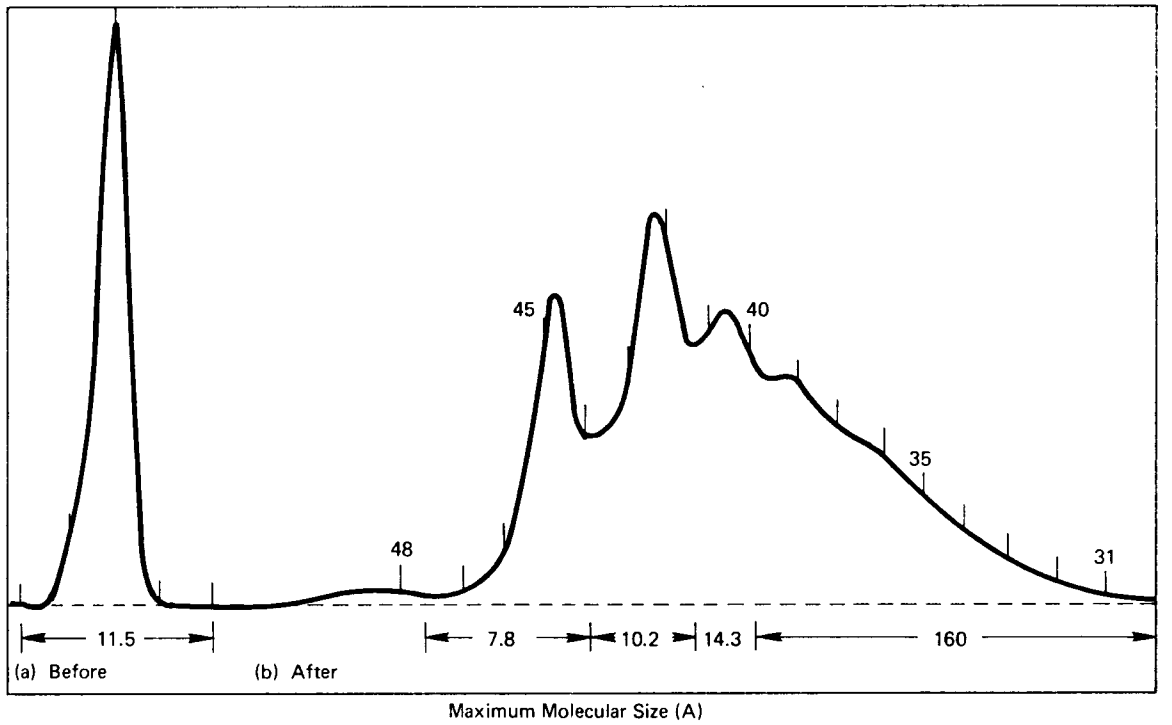


Figure 36. GEL PERMEATION CHROMATOGRAPHIC SCANS SHOWING THE MOLECULAR DISTRIBUTIONS OF ACENAPHTHALENE BEFORE AND AFTER POLYMERIZATION BY HEATING AT 300°C FOR APPROXIMATELY 14 HOURS.

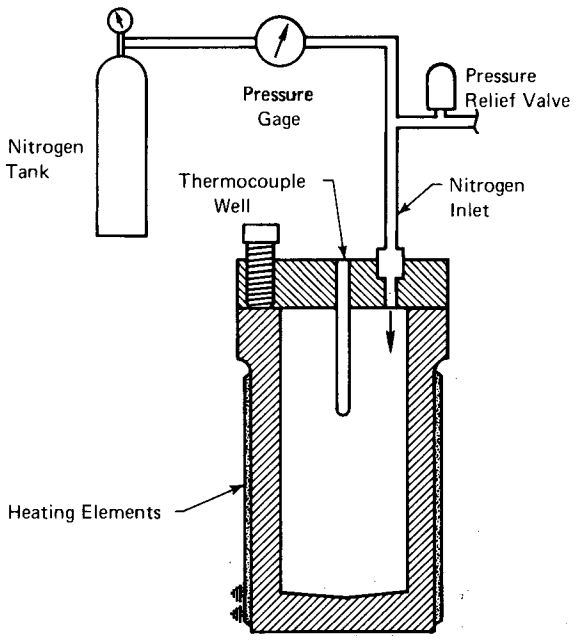


Figure 37. GAS-PRESSURE AUTOCLAVE USED IN PREPARING CINNAMYLIDENEINDENE POLYMERS.

Coke yields obtained for the various CAI polymers are shown as a function of the autoclave temperature in Figure 40. In general, coke yields of 300°C-polymerized samples appeared to be somewhat lower than those polymerized at higher or lower temperatures. It is significant that increases were observed for all samples when heated at temperatures above 300°C. This additional increase in the coke-yield value would justify the use of the higher heat-treatment temperature (~ 340°C).

Figure 41 gives a graph of the g factor of carbons derived from polymers (with two-hour heat-treatment times) as a function of the autoclave temperature. At present, no significance can be associated with the inflections in the curves. However, it is quite apparent that

air-cured samples of CAI polymers produce carbon that is less graphitic than that resulting from no air cure. Additional data will be necessary to substantiate the apparent correlation between the g factor and the autoclave temperature.

For samples polymerized at 300°C, changes in the average molecular weight with time are indicated in Figure 42. The polymer apparently degraded during the initial six to eight hours; and, subsequently, increased in molecular weight after eight to ten hours.

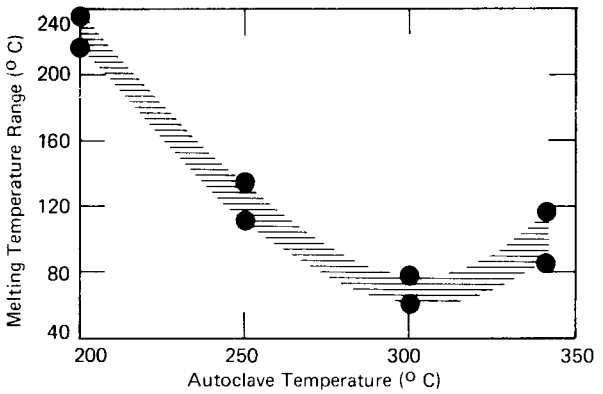


Figure 38. MELTING TEMPERATURE RANGE OF AUTOCLAVE-POLYMERIZED (SIX HOURS) CINNAMYLIDENEINDENE AS A FUNCTION OF THE AUTOCLAVE TEMPERATURE.

Effects of the autoclave temperature and time on the resulting microstructures did not appear significant. However, the effect of an air cure was pronounced, as can be seen from the microstructures of samples that were carbonized both with and without an air cure. This approach will possibly afford some control over the carbon properties derived from CAI polymers.

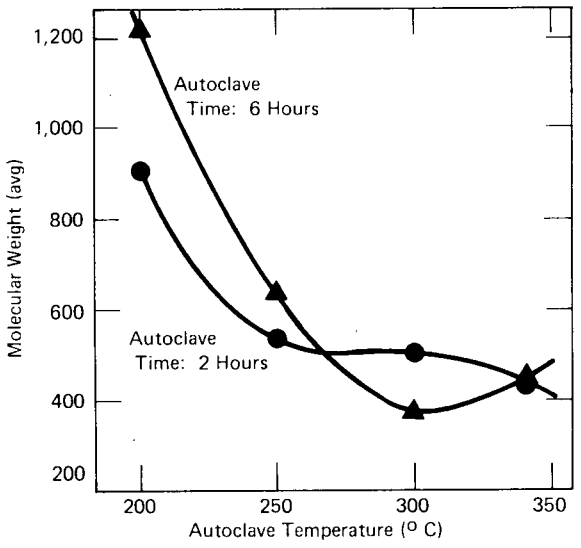


Figure 39. AVERAGE MOLECULAR WEIGHT OF AUTOCLAVE-POLYMERIZED CINNAMYLIDENEINDENE AS A FUNCTION OF THE AUTOCLAVE TEMPERATURE.

CAI-Potassium Effects - Including certain potassium compounds in CAI significantly influenced the properties of the derived carbon.[13] This fact was quite apparent for CAI products which were produced using potassium hydroxide as a reactant. Data on properties of carbon derived from a series of CAI samples containing potassium hydroxide are given in Table 15. Concentrations of potassium hydroxide are expressed in terms of their potassium content, as determined by X-ray fluorescence methods. Variation in the potassium content was obtained by varying the purification procedures which consisted of washing CAI products with methanol or methanol/acetic acid solutions. Decreases in graphiticity with an increasing potassium content is apparent in Table 15 as evidenced by changes in the interlayer spacing and crystallite size. These changes are shown as a function of the potassium content in Figure 43. Though these values appeared to approach constancy at 4,000 to 5,000 ppm potassium, the very low crystallinity of the sample containing 8,370 ppm potassium suggests that much lower g-factor values would be obtained for samples containing 4,000 to 8,000 ppm potassium.

Table 15

PROPERTIES OF CARBONS DERIVED FROM CINNAMYLIDENEINDENE SAMPLES WITH A VARIABLE POTASSIUM CONTENT

Sample Number	Potassium Content(1) (ppm)	d_{004} (A)	g Factor	L_c (A)
H2-58A	8,370	-	-	-
H2-58B	4,320	1.6931	0.635	97
H2-58C	3,920	1.6931	0.635	97
H2-58D	3,590	1.6917	0.671	105
H2-58E	1,660	1.6885	0.742	122
H2-47B	690	1.6860	0.800	153
H2-56D	40	1.6825	0.882	203

(1) Potassium present as potassium hydroxide; measured by X-ray fluorescence.

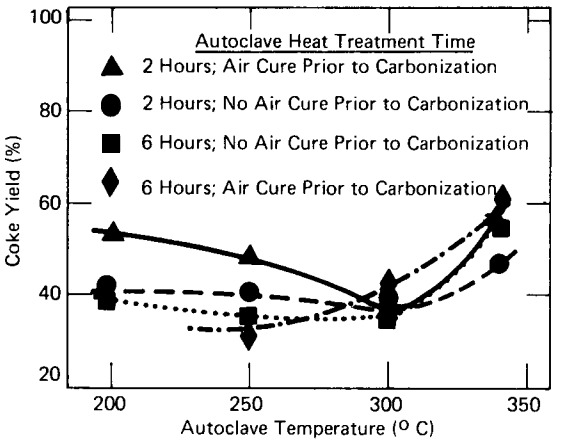


Figure 40. COKE YIELDS (AFTER 1,000°C) OF AUTOCLAVE-POLYMERIZED CINNAMYLIDENEINDENE AS A FUNCTION OF THE AUTOCLAVE TEMPERATURE.

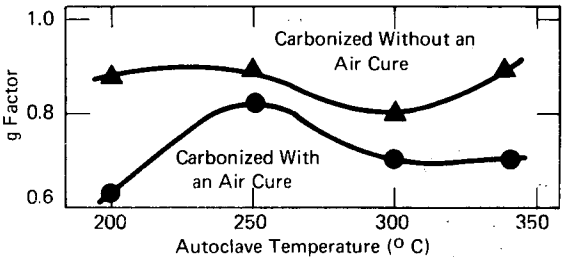


Figure 41. CORRELATION OF THE g FACTOR OF CARBONS (AFTER 2,800°C) DERIVED FROM AUTOCLAVE-POLYMERIZED CINNAMYLIDENEINDENE AS A FUNCTION OF THE AUTOCLAVE TEMPERATURE. (Autoclave Heat-Treatment Time was Two Hours)

An indication of the crystallinity of the carbon samples can be seen in Figure 44. The very evident change in microstructure with increasing potassium content corresponds favorably to the X-ray diffraction data given in Table 15. These microstructural changes strongly suggest that potassium hydroxide can be used to effectively modify the properties of the CAI-derived carbon. However, such an approach to the control of carbon properties would be limited to those applications which can tolerate a residual potassium content.

Why certain potassium compounds influence carbon properties cannot be completely explained at present. However, thermal studies indicate that fusion and polymerization temperatures are lowered somewhat by the presence of potassium hydroxide, and that the depression in temperature increases with increasing potassium hydroxide content. Differential thermal analysis curves for two of the samples listed in Table 15 may be compared in Figure 45. A shift in temperature corresponding to the fusion and polymerization steps is evident. Also significant is the low intensity of the melting endotherm for the 8,370-ppm sample. This fact suggests that polymerization begins soon after the fusion process begins, and the simultaneous process would result in an association of lower intensities with both the exothermic and endothermic processes.

Potassium compounds other than the hydroxide were evaluated by adding the compounds by wet or dry blending to CAI containing < 100 ppm potassium. Some of these potassium compounds influence the properties of the CAI-derived carbon while others have little or no effect. Data for the CAI samples containing potassium acetate are listed in Table 16. These samples were prepared by forming a slurry of CAI in methanol/potassium acetate solutions of varying concentrations.

Data in Table 16 suggest an increase in the coke yield with increasing potassium content. This fact is again an indication that polymerization is enhanced by certain potassium compounds, and changes observed in corresponding carbons suggest that crosslinking polymerization modes are promoted and enhanced by these compounds. If so, crosslinking increases with the potassium content; which, in turn, inhibits the molecular alignment prior to pyrolysis and thus inhibits subsequent crystallization. Decreases in graphiticity with increasing potassium content that are indicated in Table 16 coincide with the microstructural changes which are quite similar to those observed for the CAI-potassium hydroxide mixtures.

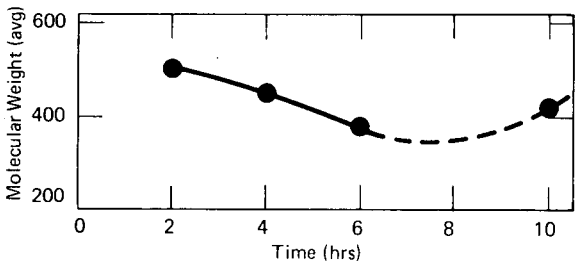


Figure 42. AVERAGE MOLECULAR WEIGHT OF AUTOCLAVE-POLYMERIZED (AT 300°C) CINNAMYLIDENEINDENE AS A FUNCTION OF THE AUTOCLAVE HEAT-TREATMENT TIME.

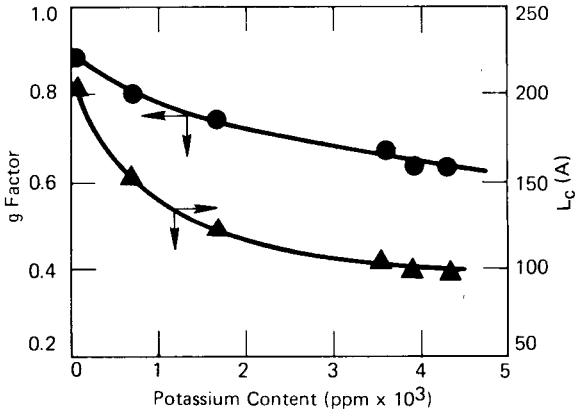


Figure 43. CRYSTALLITE SIZE (L_c) and g FACTOR OF CARBONS (AFTER 2,800°C) DERIVED FROM CINNAMYLIDENEINDENE SAMPLES WITH A VARIABLE POTASSIUM CONTENT.

Microstructures from three additional CAI/potassium compound blends were studied. Microstructures of samples derived from CAI/potassium hydrogen phthalate mixtures decrease in graphiticity with increasing potassium content. It appears, however, that this potassium compound is somewhat more effective in modifying properties than potassium hydroxide or potassium acetate, since corresponding microstructural changes occur at lower potassium levels. The same observation was made for CAI samples containing potassium nitrate. In the CAI/potassium acetate samples, potassium contents of approximately 2,000 ppm result in carbon with a fine-grain, uniform texture. For CAI/potassium hydroxide samples, approximately 4,000-ppm potassium concentrations were required to produce this type of carbon.

Table 16

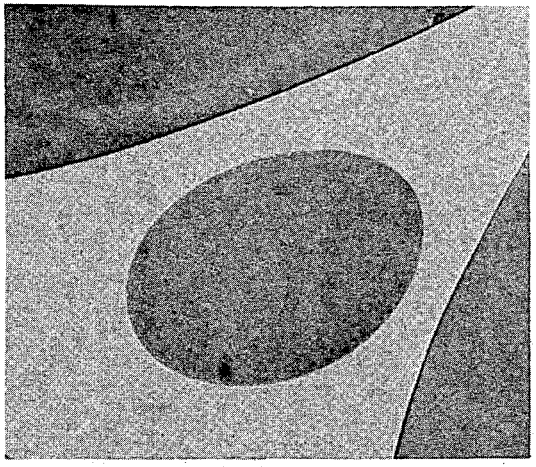
PROPERTIES OF CARBON DERIVED FROM CINNAMYLIDENEINDENE CONTAINING VARIOUS QUANTITIES OF POTASSIUM

Sample Number	Potassium Content(1) (ppm)	Coke Yield (%)	d_{004} (A)	g Factor	L_c (A)
D	700	39	1.6871	0.776	135
F	2,720	39	1.6914	0.671	99
C	4,060	41	1.6943	0.600	95
B	15,000	45	Nongraphitic		

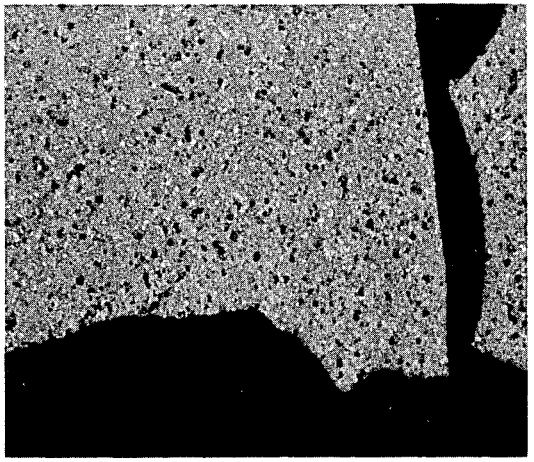
(1) Potassium present as potassium acetate. Samples of cinnamylideneindene were slurried in methanol solutions containing potassium acetate.

A fourth potassium compound observed to influence the properties of CAI-derived carbon was potassium carbonate. Observed correlations between the microstructural properties and potassium contents were similar to those observed for the CAI/potassium hydroxide mixtures.

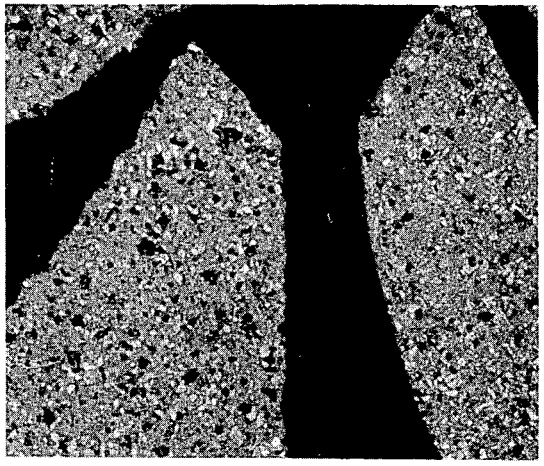
Other potassium compounds that were evaluated had little or no influence on the



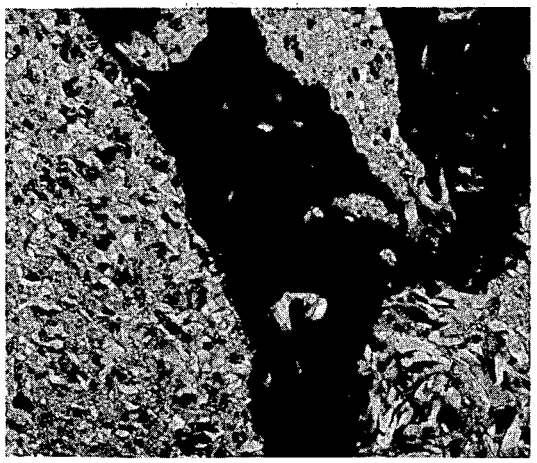
(a) 8,370 ppm. G747-1



(b) 4,320 ppm. G747-3

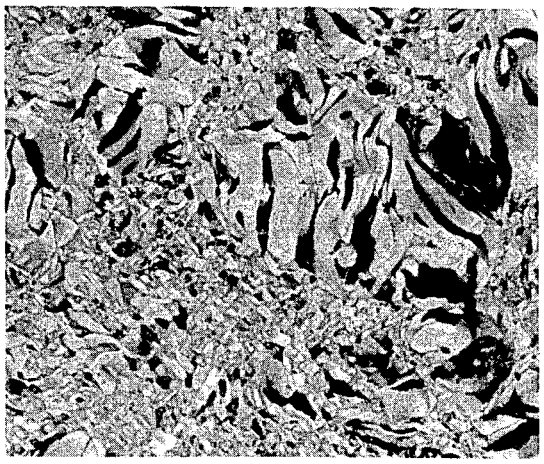


(c) 3,590 ppm. G743-6



(d) 1,660 ppm. G747-7

(e) 690 ppm. G623-2



(f) 40 ppm. G749-13

Figure 44. MICROSTRUCTURES OF CARBONS (AFTER 2,800°C) DERIVED FROM CINNAMYLIDENEINDENE CONTAINING VARIOUS QUANTITIES OF POTASSIUM HYDROXIDE.

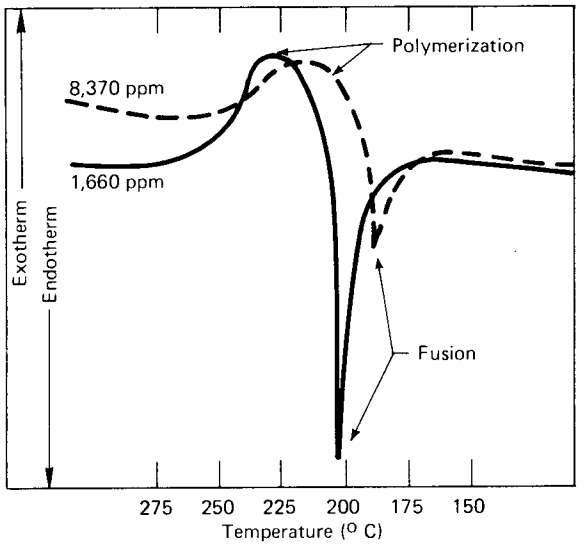


Figure 45. DIFFERENTIAL THERMAL ANALYSIS SCANS OF CINNAMYLIDENEINDENE SAMPLES WITH VARIOUS POTASSIUM CONTENTS. (Heating Rate, 6°C/min)

carbon properties. These materials, along with the upper limit of the range of potassium concentrations that were evaluated are: potassium chloride (4,220 ppm), potassium phosphate (3,340 ppm), potassium sulfate (2,030 ppm), and potassium oxalate (1,360 ppm). At higher concentrations, some of these compounds could produce results similar to those discussed previously. Collectively, the data indicated that changes in the carbon properties due to the inclusion of potassium compounds in the CAI precursor varied with the choice of the specific potassium compound; and, thus, the potassium concentrations associated with the given property changes (if any) would be different for each potassium compound.

Impregnation Procedure - Liquid impregnation of the graphites was achieved by melting CAI-340 polymer under vacuum in contact with the graphite while increasing the temperature to approximately 125°C.[10] The vacuum operation was maintained at temperature for approximately two hours and then the system was pressurized to ambient pressure. The experimental graphite was submersed in the liquid CAI polymer during this operation. Both the submersed graphite and excess CAI polymer were then transferred to a second unit for pressure application.

The pressure autoclave was heated to 180°C and a pressure of 4,500 psi was applied to the polymer-graphite body for 16 hours. Amounts of pressure, temperature, and hold time were arbitrarily selected. This procedure was found to be very effective in filling all of the available open pores of the graphite.

After the pressure cycle, the polymer-graphite body was transferred to a coking furnace and heated to a maximum of 850°C, using a heating rate of 2 hours to 200°C, a rate of 15°C per hour from 200 to 500°C, and 30°C per hour from 500 to 850°C. The graphite was reimpregnated after baking to 850°C if a further density increase was required. Ultimately, the graphite was fired to 2,800°C prior to determining its physical properties.

Densification - The degree of densification of several graphites is reported in Table 17.[14] These data show that when the CAI polymer and procedure are used effectively, the density of a variety of graphite types increases. Although the final density is dependent on many variables, densities of 1.87 to 2.02 gms/cc were achieved. The carbon weight increases show that the CAI polymer essentially filled all of the open porosity during each impregnation. A carbon yield of approximately 50 percent was obtained. Each successive impregnation increased the density by about one half of that achieved in the preceding impregnation.

Table 17

DENSITY CHANGE FROM LIQUID IMPREGNATION OF MOLDED GRAPHITES

Graphite Number[1]	Filler	Binder	As-Molded Density (gms/cc)	Density after Number of Impregnations (gms/cc) 1	2	3	4	5	Fired Final Density[2] (gms/cc)
131	PCD-0Q	CAI	1.68	1.77	1.85	1.90	1.93	-	1.92
133	PCD-0Q	CAI	1.70	1.84	1.87	1.93	-	-	1.92
141	PCD-0Q	CAI	1.68	1.80	1.88	1.93	-	-	1.93
143	PCD-0Q	CAI	1.70	1.85	1.91	1.93	-	-	1.93
134	PCD-0Q	ITX	1.80	1.88	1.90	1.93	-	-	1.93
135	PCD-0Q	ITX	1.76	1.84	1.86	1.89	-	-	1.88
144	PCD-0Q	ITX	1.79	1.86	1.89	1.93	-	-	1.93
170	PCD-0Q	ITX	1.79	1.81	1.87	1.88	1.91	-	1.91
171[3]	PCD-0Q	ITX	1.66	1.74	1.77	1.77	1.77	-	1.91
163	PCD-0Q	350 Pitch[4]	1.82	1.89	1.93	1.94	-	-	1.94
147	PCD-0Q + 1% Rayon Fibers	ITX	1.82	1.93	1.95	1.96	-	-	1.96
148	PCD-0Q + 1% Phenolic Fibers	ITX	1.83	1.93	1.98	2.00	-	-	1.99
169	PCD-9 (900° C fired powder)	ITX	1.76	1.84	1.85	1.91	1.94	1.94	1.94
140	ITX	ITX	1.87	1.96	1.99	2.02	-	-	2.02
156	ITX	ITX	1.86	1.94	1.98	2.00	-	-	2.00
162	ITX	ITX	1.86	1.94	1.99	2.00	-	-	1.99
150	CAI (~ 300 ppm K)	ITX	1.74	1.83	1.90	1.94	-	-	1.94
152	CAI (~ 300 ppm K)	ITX	1.73	1.82	1.89	1.90	1.92	-	1.91
157	CAI (~ 300 ppm K)	ITX	1.69	1.80	1.87	1.93	-	-	1.92
167	CAI (~ 300 ppm K)	ITX	1.67	1.78	1.79	1.87	1.91	1.92	1.91
154	CAI (~ 300 ppm K)	CAI	1.60	1.76	1.84	1.85	1.87	1.88	1.87
155	CAI (~ 300 ppm K)	CAI	1.61	1.75	1.84	1.89	1.93	-	1.93
158	CAI (~ 300 ppm K)	CAI	1.58	1.75	1.82	1.88	1.90	1.91	1.91

(1) All graphites molded at 1,400° C and 1,600 psi using 25 pph of binder except where noted. The graphites were fired to 2,800° C, without pressure, before impregnation except for Graphite 171. All fillers were low-fired carbons (1,000° C) except for Graphite 169.

(2) Temperature at 2,800° C.

(3) Not fired to 2,800° C prior to impregnation.

(4) 35 pph binder.

Most of the impregnated graphites show that the density increased in a uniform manner. However, some did exhibit irregularities in the rate of densification. In two of these cases, the irregular fill rate was due to the fact that the CAI polymer had been previously used. (The CAI polymer, as do most of the thermoplastic resins, will change in melting point and viscosity by repeated heating under vacuum at 125°C. The increased melting point and viscosity decreases the effectiveness of the polymer as an impregnant.)

The other irregularities in the rates of densification were due to problems associated with the vacuum operation. In all of these cases, during evacuation, excessive air outgassing of the CAI polymer before reaching 125°C caused the material to flow from around the graphite body. The graphite was not completely submersed after evacuation and, therefore, not fully impregnated. In all cases, they were carbonized to 850°C prior to reimpregnation.

Physical Properties - As part of the graphite fuel-element development program, molded graphites were made to obtain physical property data on different carbon fillers.[14] Several of these materials were liquid impregnated with CAI polymer to obtain data on the effect of this operation. All impregnated graphites were prefired to 2,800°C prior to impregnation. Physical properties of the graphites are tabulated in Table 18; photomicrographs of impregnated and nonimpregnated graphites are presented in Figures 46 and 47.

Density - The initial bulk density was dependent on the type of filler and binder used in the manufacturing process. In general, densities of 1.76 to 1.88 gms/cc were obtained in the molded state. Densities of 1.91 to 2.02 gms/cc were obtained for graphites that had been liquid impregnated.

Porosity - All of the graphites were prepared using a graphitizable resin binder, and an open porosity of 17 to 22 percent was obtained. The average pore entrance diameter was small, usually less than two micrometers. The impregnated pieces had reduced open porosities (~ 10%) and reduced pore entrance diameters. Typical mercury porosimetry data are given in Table 19.

Electrical Resistance - Considerable variation in the electrical resistance can be expected since the type of carbon filler and binder was varied in these studies. The effect of impregnation on the resistivity is consistent inasmuch as the resistivity decreased in all cases when the density was raised by impregnation. The extent of the decrease, however, as a function of the degree of densification is not comparable for all of the graphites. Electrical resistance data can be used as a very accurate method for determining the degree of isotropy and agrees very well with BAF data obtained by X-ray techniques. It is an accurate and an inexpensive test for this property.

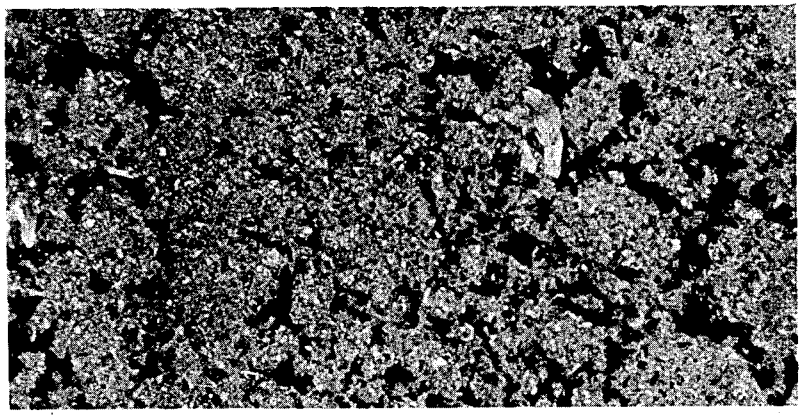
Coefficient of Thermal Expansion - All of the fillers studied during this program produced high CTE graphites with values ranging up to a maximum of 7.4 x 10^{-6}/°C (25 - 1,000°C range). The CTE values are primarily related to the filler carbon. Essentially, no change was detected that could be attributed to the three binders used in these studies. The three binders, however, were selected and the carbon derived from each of the binders was about the same type: ie, well-graphitized carbon. Using other binders could produce a change in the CTE values, but they would probably not be increased to any substantial amount and may be decreased if a glassy-type carbon was used.

Effect of the impregnation on the CTE values appeared to be small, but consistent. A slight decrease was noted in almost all cases, but the impregnant was also selected and was of a very crystalline, anisotropic carbon structure.

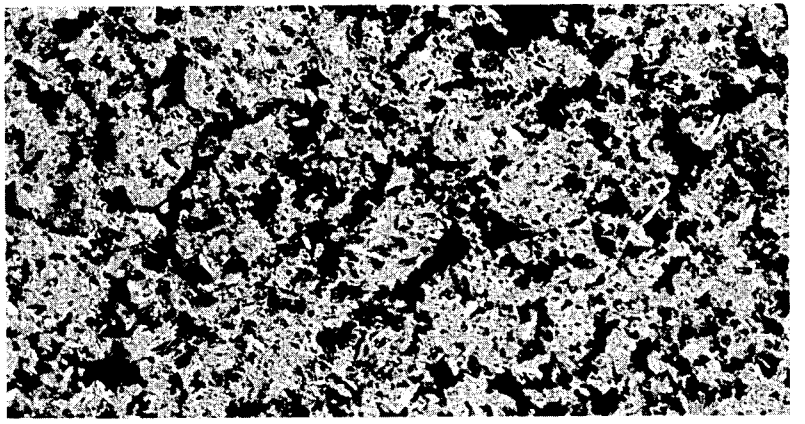
Isotropy - Most of the graphites produced a nearly isotropic body (~ 1.03 typical). Impregnation with CAI polymer produced only a small effect on the anisotropy of the near isotropic graphites. The graphites become slightly anisotropic, when impregnated, which is consistent with the CTE data. The few anisotropic graphites showed a large increase in anisotropy after impregnation. Isotropic values were determined by electrical resistance ratio data and by X-ray diffraction data. Physical property data were measured in both directions (Table 18), and the isotropic value can also be established from these data.

Graphite Number	Filler[1]	Binder	Impregnated	D (g	Electrical Resistance (μΩ-cm)			BAF (X-ray Diffraction)
				Bulk	WG	AG	Ratio	
130	PCD-0Q	CAI	No	1.70	,725	1,770	1.03	1.03
131	PCD-0Q	CAI	Yes	1.91	,290	1,305	1.01	1.02
143	PCD-0Q	CAI	Yes	1.91	,370	1,415	1.03	1.03
132	PCD-0Q	ITX	No	1.78	,350	1,395	1.03	1.02
135	PCD-0Q	ITX	Yes	1.87	,300	1,330	1.02	1.04
166[4]	PCD-0Q + 4% Rayon	ITX	No	1.80	,295	1,370	1.06	1.05
146	PCD-0Q + 1% Rayon	ITX	No	1.80	,400	1,470	1.05	1.05
149	PCD-0Q + 1% Phenolic	ITX	No	1.83	,290	1,335	1.04	1.04
148	PCD-0Q + 1% Phenolic	ITX	Yes	1.99	,125	1,215	1.08	-
161[4]	PCD-0Q	350 Pitch	No	1.79	,340	1,360	1.02	1.03
163[5]	PCD-0Q	350 Pitch	Yes	1.92	,175	1,275	1.09	-
168	PCD-9	ITX	No	1.76	,460	1,510	1.03	-
169[4]	PCD-9	ITX	Yes	1.94	,245	1,310	-	-
151	CAI (< 300 ppm K)	ITX	No	1.73	,170	1,750	1.49	1.36
152	CAI (< 300 ppm K)	ITX	Yes	1.91	940	1,560	1.66	-
153	CAI (< 300 ppm K)	CAI	No	1.58	,870	2,295	1.22	1.19
158	CAI (< 300 ppm K)	CAI	Yes	1.90	,105	1,560	1.40	-
165	CAI (2,900 ppm K)	ITX	No	1.82	,505	1,600	1.07	1.09
138	ITX	ITX	No	1.88	,110	1,245	1.12	1.09
162	ITX	ITX	Yes	1.99	970	1,135	1.17	-
164	GLC 1076	ITX	No	1.71	,400	1,380	0.99	1.04
	JA-5, As Received	-	-	1.56	,290	1,305	1.01	1.03
	ATJS, As Received	-	-	1.85	840	1,095	1.30	1.23

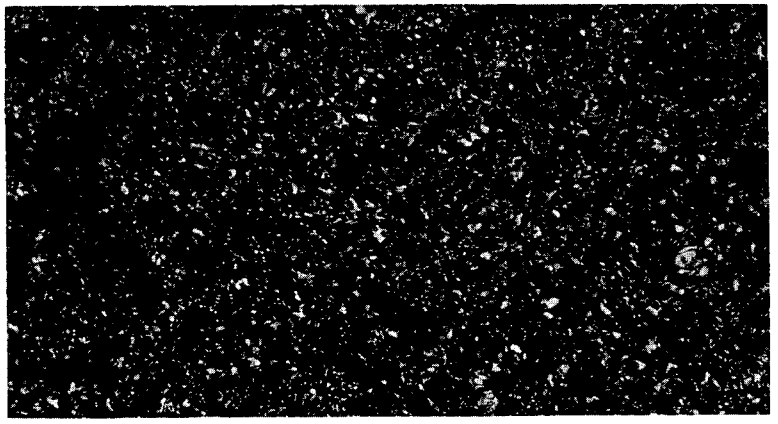
(1) All fillers were low-fired carbons (1,000° C) except where noted. The graphite 00° C. All were impregnated with CAI polymer after the 2,800° C firing temperature and were again fired to 2,800°
(2) WG - with grain; AG - across grain.
(3) Temperature - 20 to 1,000° C.
(4) 30 pph binder.
(5) 35 pph binder.



(a) PCD-9 Filler and ITX Binder. (density, 1.76 gms/cc) H495-7

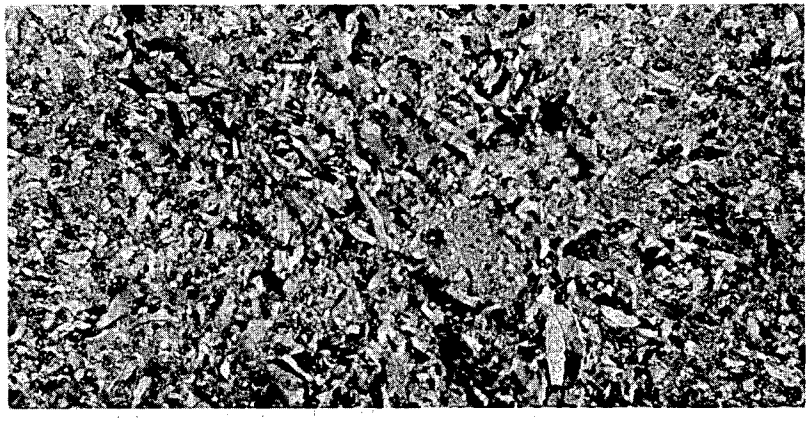


(b) GLC 1076 Filler and ITX Binder. (density, 1.71 gms/cc) H359-2



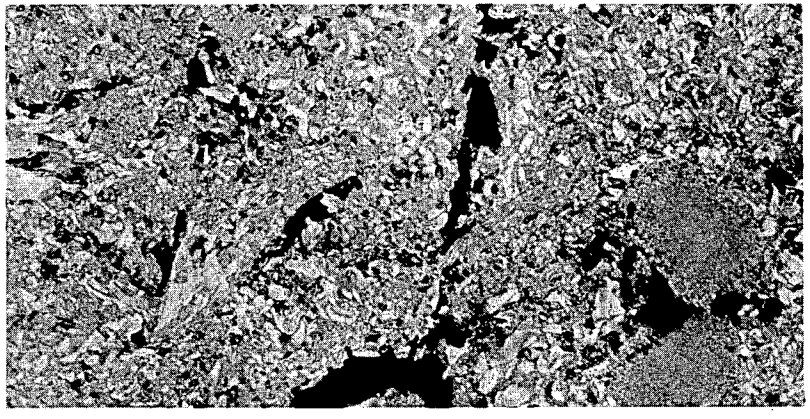
(c) CAI Filler (2,900 ppm K) and ITX Binder. (density, 1.82 gms/cc) H359-3

Figure 46. NONIMPREGNATED EXPERIMENTAL GRAPHITES. (250X)



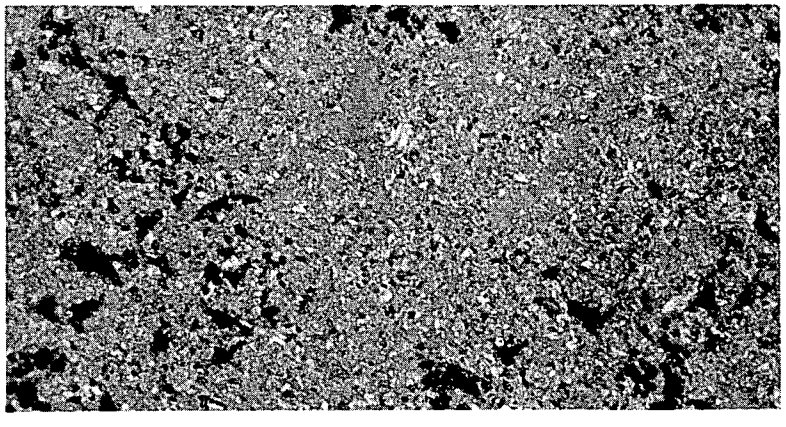
H495-4

(a) CAI Filler (< 300 ppm K), CAI Binder, and CAI Impregnant. (density, 1.90 gms/cc)



H495-5

(b) ITX Filler, ITX Binder, and CAI Impregnant. (density, 1.99 gms/cc)



H495-6

(c) PCD-0Q Filler, 350 Coal-Tar Pitch Binder, and CAI Impregnant. (density, 1.92 gms/cc)

Figure 47. IMPREGNATED EXPERIMENTAL GRAPHITES. (250X)

Table 19

POROSITY DATA FOR TYPICAL GRAPHITES

Graphite Number	Filler	Binder	Density (gms/cc) Bulk	Density (gms/cc) Liquid	Accessible Porosity (%)	Average Pore Diameter (μm)
		Nonimpregnated Graphites				
130	PCD-0Q	CAI	1.70	2.17	21.9	1.2
132	PCD-0Q	ITX	1.78	2.14	17.4	2.0
146	PCD-0Q + 1% Rayon Fibers	ITX	1.80	2.14	17.3	1.1
149	PCD-0Q + 1% Phenolic Fibers	ITX	1.83	2.15	15.1	1.6
161	PCD-0Q	350 Pitch	1.79	2.11	15.9	1.0
151	CAI	ITX	1.73	2.22	22.1	1.3
153	CAI	CAI	1.58	2.26	30.9	1.2
138	ITX	ITX	1.88	2.20	14.0	1.3
		Impregnated Graphites				
131	PCD-0Q	CAI	1.91	2.18	12.8	1.0
135	PCD-0Q	ITX	1.87	2.15	13.7	1.2
148	PCD-0Q + 1% Phenolic Fibers	ITX	1.99	2.13	6.3	1.2
163	PCD-0Q	350 Pitch	1.92	2.12	9.7	0.8
152	CAI	ITX	1.91	2.20	13.0	0.9
158	CAI	CAI	1.90	2.21	14.7	1.2
162	ITX	ITX	1.99	2.19	9.6	1.8

Flexural Strength - The most variable property found in these studies was the flexural strength. In general, flexural strengths of 3,000 to 5,000 psi were obtained on isotropic graphites in the as-molded state. Liquid impregnation was performed on graphitized pieces and produced inconsistent results. The strength of a graphite made with PCD-0Q filler and ITX binder was not changed by densification, but the same filler bound with CAI showed an increased flexural strength when densified. The strength of a graphite made with ITX filler and ITX binder was not changed by densification, but a CAI filler bound with CAI increased in strength when densified by infiltration.

Densification of graphites prepared from PCD-0Q filler and 350 coal-tar pitch showed an increased flexural strength. The highest-strength graphite was made by using PCD-0Q filler, one percent phenolic fibers, and ITX binder. When densified, this graphite had a with-grain flexural strength of 9,200 psi.

Typical flexural strength data of impregnated and nonimpregnated graphites are also listed in Table 18.

Modulus - Typical modulus values for the graphites ranged from 0.9 to 1.6 x 10^6 psi and were dependent on the filler, density, binder, and other variables. In all cases, high-density graphites (> 1.95 gms/cc) were prepared having modulus values of less than 1.6 x 10^6 psi. These data are also reported in Table 18.

Strain at Rupture - Percent strain-at-rupture values for the graphites were measured. These data are also included in Table 18. Except for one graphite, all values ranged from 3,700 to 7,300 μin/in. All measurements were made by strain-gage techniques on the flexural sample at room temperature.

GL 1076 Flour - Data included in Table 18 for the graphite molded from low-fired GL 1076 flour (Graphite 164) show that this graphite had a slightly lower density, flexural strength, and modulus than did a graphite fabricated from PCD-0Q flour (Graphite 132). Other properties, including the CTE, are essentially the same as those for PCD-0Q graphite.

Commercial JA-5 Graphite - This material, received in bulk form (Airco Speer Carbon-Graphite), had a low bulk density and was nearly isotropic. The graphite had good strength and low electrical resistivity. The modulus was low and the strain at rupture high. Property data are provided in Table 18.

Commercial ATJS - This material (Carbon Products Division—Union Carbide Corporation) was selected because of its excellent thermal shock properties. The material was characterized using the same procedure as that used for the experimental graphites. The properties recorded in Table 18 show that the material was anisotropic. A density of 1.85 gms/cc was measured on the test specimens. The strength was 5,100 psi (with grain), and a modulus of 1.7×10^6 psi was measured. The strain at rupture was 3,800 μin/in (with-grain direction).

Microstructure of Graphites - The microstructure of all experimental graphites was examined using standard metallographic techniques. Six typical photomicrographs representing both impregnated and nonimpregnated graphites are contained in Figures 46 and 47.

CONCLUSIONS

These impregnation studies have demonstrated that NERVA fuel element matrices can be carbon impregnated by gaseous and liquid processes. Both types of gaseous processes were shown to be effective.

GASEOUS IMPREGNATION

Direct Flow

This process involved passing an argon-methane gas mixture around the NERVA fuel elements at temperatures up to 950°C. Methane gas penetrated the open porosity of the matrix structure and was, subsequently, decomposed into carbon. Impregnation times of more than 100 hours were required to obtain density changes ranging from 1.70 to 1.90 gms/cc. Flexural strengths of the fuel element were shown to be increased from an average of 5,600 psi (density of 1.70 gms/cc) to 8,100 psi (density of 1.84 gms/cc).

Pulse Vacuum

This process employed an evacuation of the fuel element matrices and backfilling them to 2 psig with 1,3-butadiene gas at a process temperature of 750°C. The butadiene gas was decomposed into carbon. Impregnation times of 10 to 30 hours produced density changes ranging from 1.70 to 1.90 gms/cc. The physical properties of the graphite fuel element were shown to be progressively improved with an increased density. A tensile strength of a nonimpregnated body (having a density of 1.72 gms/cc) was typically 3,000 to 5,000 psi. When densified to a density of 1.90 gms/cc, an increased tensile strength of about 8,500 psi was obtained. The densified matrices also showed a significant increase in thermal stress resistance when tested using a welder-type thermal stress test. The pulse-vacuum system was scaled in size to permit pilot-plant studies to be conducted.

LIQUID IMPREGNATION

All liquid impregnation studies used a polymer of cinnamylideneindene which was well characterized in order to define and control the type of carbon deposited in the graphite pores. This polymer produced a very graphitic, anisotropic-type carbon when heated to 2,800°C. Bulk density changes ranging from 1.70 to 1.90 gms/cc were obtained by the use of two to four liquid impregnation cycles. In all cases, the open pores were decreased from 20 to 12 percent when densified. In most experiments, the flexural strengths were increased by densification. In all cases the electrical resistance of the impregnated graphites was lower than the electrical resistance of the nonimpregnated body. A variety of graphite types was successfully densified using the liquid impregnation procedure.

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